TEXTILE SOAPS AND OILS

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A HANDBOOK

ON THE

PREPARATION, PROPERTIES, AND ANALYSIS OF THE SOAPS AND OILS USED IN TEXTILE MANUFACTURING, DYEING, AND PRINTING

BY

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AUTHOR OF "SOAPS," "LUBRICATING OILS, FATS, AND GREASES," "COLOUR," ETC.

SECOND EDITION, REVISED AND PARTLY RE-WRITTEN

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WITH ELEVEN ILLUSTRATIONS

LONDON

AUTHOR'S PREFACE TO FIRST EDITION.

SOAPS and oils are very largely used in the manufacture of textile fabrics from cotton, wool, silk, and other fibrous materials, and in the arts of dyeing and printing those fabrics. It has been thought, therefore, that a small handbook which would describe the preparation, properties, uses and analyses of these useful, substances would be of use to every person concerned in their preparation and use; hence the appearance of this little book. In writing it, the author has kept in view the practical side of the subject, and tried to gather together that information which would be of most value in the practical application of the soaps and oils.

Those readers who may desire further information regarding the materials and methods of manufacture are referred to the author's large book on "Soaps". As regards oil, there is one use of these bodies in the textile trades which is not referred to here, and that is in the lubrication of the machinery. This subject will be found dealt with in the author's book on "Lubricating Oils, Fats, and Greases".

<div style="text-align:right">G. H. H.</div>

1904.

REVISER'S PREFACE.

ALTHOUGH it is only some ten years ago since the first edition of this work was published, yet during this time considerable progress has taken place in the manufacture of soaps, and in the methods of soap and oil analysis, so that whilst it has been endeavoured as far as possible to maintain the same general character of the book as in the first edition, it has been considered desirable to re-write certain portions, notably that dealing with the methods of soap manufacture, and to considerably expand those detailing the more simple processes for the analysis of textile soaps and oils.

<div align="right">W. H. S.</div>

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TEXTILE SOAPS.

I. INTRODUCTORY.

SOAP is very largely employed in every branch. of the textile industries. In the silk industry, it has been used for centuries in the degumming or boiling off of the raw silk, and in many processes of silk-dyeing; in the woollen trades, it is used in the operations of milling, or fulling, and felting of woollen fabrics, and in the scouring and cleaning of wool. In the cotton trade, it is employed in a great variety of ways: in the dyeing and printing of cotton fabrics, in cotton-finishing, and, to a limited extent, in the bleaching and cleaning of cotton. In the working of linen, jute, hemp, China grass, etc., soap is used in several ways. The work that soap has to do, and the objects for which it is employed in these industries, vary very much; so that it is found that a soap which is the most suitable for scouring woollens will not be suitable for use in calico-printing, or in boiling-off silk. The special features of the most suitable soaps for each of these purposes are discussed later on.

There are two kinds of soap found in commerce, hard soap and soft soap, and both kinds are used in the textile trades.

Soap is made from such fats and oils as tallow, lard, olive oil, palm oil, cocoa-nut oil, bone tallow, castor oil, etc.,—all of which are derived from the animal or vegetable kingdoms. There is a great similarity in the composition of these fatty bodies. They belong to the large group of chemical compounds known as salts, although they differ so markedly in appearance from typical members of the salt series like common salt, Epsom salts, copperas, bluestone, Glauber's salt, etc. Salts are formed essentially by the combination of an acid and a base; the char-

acteristic features of each being neutralized, and a new compound
with different properties being obtained. In the case of the salts
of which oils and fats consist, these all have one common base,
a trihydric alcohol termed glycerine or glycerol, combined, how-
ever, with a great variety of acids, few oils containing less than
two, while in others—cocoa-nut oil, palm-nut oil, and butter, for
example—there is a much greater number present.

It is a well-marked feature of chemical activities that bases
vary much in strength, and that a strong base will remove a
weak base from its combinations; thus, for instance, if to a
solution of copper sulphate one of caustic soda be added, the
latter, being a stronger base, displaces the copper from its
combination with the sulphuric acid, and sodium sulphate is
formed in solution and copper hydroxide precipitated out. And
so with acids, a strong acid will displace a weaker acid—a pro-
perty taken advantage of in the manufacture of acetic acid,
hydrochloric acid, and nitric acid, by the action of sulphuric
acid—a stronger acid—on sodium acetate, sodium chloride, or
sodium nitrate respectively. When oils and fats are boiled with
a solution of caustic soda or potash, the soda or potash takes out
the fatty acid or fatty acids from the oil or fat, and the product
thus obtained forms the familiar article soap—hard soap if
caustic soda is used; soft soap if caustic potash is employed.
The base glycerol separates out, and forms, in the case of hard
soaps, a valuable by-product. This operation of making soap
is termed " saponification," and all oils which can thus be trans-
formed into soap are called " saponifiable oils ".

The fatty bodies, on account of their always yielding glycerine
on being saponified, are known as " glycerides " or " trigly-
cerides," and the action of the caustic soda or caustic potash—
" the alkalies," as they are called—on certain typical glycerides
is shown in the following chemical equations :—

$$CH_2OOC_{18}H_{35}$$
$$CHOOC_{18}H_{35} \quad + \quad 3NaOH \quad = \quad 3NaOOC_{18}H_{35} \quad + \quad CHOH$$
$$CH_2OOC_{18}H_{35} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_2OH$$

Stearin, or glyceryl   Caustic soda   Sodium stearate,   Glycerine
     stearate   or soap
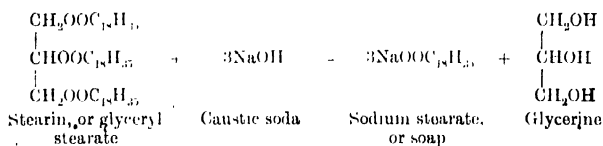
Stearin is the principal constituent of tallow and other animal fats.

$$
\begin{array}{llll}
CH_2OOC_{18}H_{33} & & & CH_2OH \\
CHOOC_{18}H_{33} & + \ 3NaOH & = \ 3NaOOC_{18}H_{33} & CHOH \\
CH_2OOC_{18}H_{33} & & & CH_2OH \\
\text{Olein, or} & \text{Caustic} & \text{Sodium oleate,} & \text{Glycerine.} \\
\text{Glyceryl oleate.} & \text{soda.} & \text{or soap.} &
\end{array}
$$
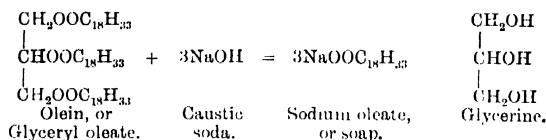
Olein is the principal constituent of olive oil and many other liquid oils of the vegetable kingdom.

$$
\begin{array}{llll}
CH_2OOC_{18}H_{31} & & & CH_2OH \\
CHOOC_{18}H_{31} & + \ 3KOH & 3KOOC_{18}H_{31} & CHOH \\
CH_2OOC_{18}H_{31} & & & CH_2OH \\
\text{Linolin, or} & \text{Caustic} & \text{Potassium linolate,} & \text{Glycerine.} \\
\text{Glyceryl linolate} & \text{potash.} & \text{or soft soap.} &
\end{array}
$$
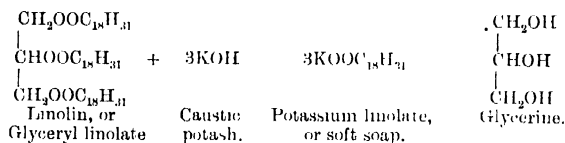
Linolin is the principal constituent of linseed oil and drying oils in general.

The formulæ given for stearin, olein, and linolin are typical formulæ, and all the glycerides have a similar composition.

When the glycerides are subjected to the action of superheated steam, they undergo what is called "hydrolysis" that is, they take up the elements of water, and the acids and the glycerine of the fat are separated, as is indicated by the chemical equation.

$$
\begin{array}{llll}
CH_2OOC_{18}H_{35} & & & CH_2OH \\
CHOOC_{18}H_{35} & + \ 3H_2O & 3HOOC_{18}H_{35} & + \ CHOH \\
CH_2OOC_{18}H_{35} & & & CH_2OH \\
\text{Stearin.} & \text{Water.} & \text{Stearic Acid.} & \text{Glycerine.}
\end{array}
$$
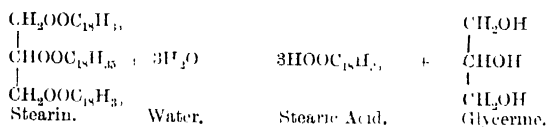
This property of the glycerides is taken advantage of in the commercial manufacture of stearic acid and glycerine.

The fats and oils used by soap manufacturers are derived from both vegetable and animal sources; none, so far known, are obtained from the petroleum oils or paraffin shales, with the exception of naphthenic acid, a product recovered in the Russian oil industry from "soda tar" obtained in refining the oil, which is used in some low-class Russian soaps.

There is no very essential difference between an oil and a fat; it is purely a question of temperature as to whether a particular body makes its appearance in a solid form, as a fat, or liquid, as an oil, at the ordinary temperature of the place in which it is. Palm oil here is a fat, i.e. solid; in Africa it is an oil, i.e. liquid. Cocoa-nut oil in this country is a white solid; in India it is a watery white liquid. Olive oil here is an oil; in Greenland it is a fat. That it is simply a question of temperature is proved by the fact that if tallow or palm-oil or cocoa-nut oil be kept in a sufficiently warm place they are converted into liquids, while on the other hand, by artificially cooling olive oil, or cotton-seed oil, or lard oil, they are solidified, and are then in no way distinguishable from a solid fat.

These few examples will suffice to show the relation between fats and oils, and in the following pages, when these bodies are generally referred to, the term fat may be taken to include the oils, and vice-versa.

There are three principal classes of oils, differing considerably both in constitution and properties. These are—

1. Fixed oils.
2. Volatile or Essential oils.
3. Mineral oils.

1. **The Fixed Oils and Fats,** which may be of animal or vegetable origin, are characterised by being lighter than water, their specific gravity ranging from 0·878, which is that of sperm oil, the lightest of natural oils, to 0·965, that of castor oil. In water they are quite insoluble; on shaking up with it they form an emulsion in which the oil is distributed throughout the body of the water in the form of minute globules; on standing, the oil gradually separates out and rises to the surface. They impart a greasy stain to paper, causing it to become more or less transparent, and this stain is permanent. They are readily soluble in ether, chloroform, carbon bisulphide, carbon tetrachloride, tetrachlorethane, trichlorethylene, benzol, turpentine, and, with the exception of castor oil, in petroleum spirit.

The solubility of the oils in alcohol varies very much; castor oil dissolves readily, linseed oil is soluble in about ten times its

volume of strong alcohol, but the solubility of tallow is only slight. A great deal depends upon the freedom of the oil from acidity, which increases its solubility in alcohol.

On being heated to 500° to 600° F. fixed oils decompose, and under ordinary atmospheric pressure they cannot be distilled. The products of decomposition are rather variable, but include water, carbonic acid, acrolein, acetic acid, sebacic acid. etc. At a reduced pressure and with the aid of superheated steam they may be distilled.

The oils are compounds of the three elements, carbon (C), hydrogen (H), and oxygen (O), arranged in the form of glycerides, as previously explained, and belonging to the fatty or chain series of organic compounds. The proportions of these three elements vary in different oils : for linseed oil these are—carbon, 77·4 per cent. ; hydrogen, 11·1 per cent. ; and oxygen, 11·5 per cent.

In addition to the glycerides, fixed oils contain a small amount, usually less than 1 per cent., of unsaponifiable matter, consisting of cholesterol in the case of animal oils, and of phytosterol in vegetable oils. On the separation and examination of the unsaponifiable matter, a useful method has been based for the detection of vegetable oils in animal oils or vice-versa. (*vide*, p. 165).

When boiled with caustic soda, caustic potash, or lime, fixed oils are decomposed and two bodies are formed, one glycerine, the other the familiar article soap. This operation is known as " saponification," as has been shown above.

On exposure to air, all oils become more or less oxidized. Some, such as olive oil and lard oil, are but slightly affected— these are known as the " non-drying oils " ; while linseed oil and some other oils, on exposure to the air, gradually become hard— " dry," as it is called ; these are known as " drying oils ". There is no hard or sharp line between these two classes of oils ; and the transition is very gradual between, say, sperm and olive oils, which are types of " non-drying oils," through cotton-seed oil, soya-bean oil, and niger-seed oil, " semi-drying oils," to linseed oil and poppy-seed oil, types of the " drying oils ". This property of drying is due to the presence of unsaturated carbon atoms,

and the drying capacity of an oil is directly· measured by the
proportion of iodine it will absorb, or its iodine value (see p. 1ƒ7).
It has, a material influence on the uses to which the oils are
put in practice : the non-drying oils find extensive use in lubri-
cating machinery; the semi-drying oils are used as food oils;
while the drying oils are used primarily as painting oils. Even
in soap-making, the drying oils are the best for making soft soap,
while the non-drying oils make the best hard soaps.

2. **The Volatile or Essential Oils** are entirely derived from
the vegetable kingdom. They also consist of carbon, hydrogen,
and oxygen, but the proportion of the latter is usually less than
in the fixed oils, and their constituents belong to the aromatic
or ring branch of organic compounds. Essential oils vary in
specific gravity very much ; some are lighter, others are heavier,
than water, in which some are slightly soluble ; most are soluble
in alcohol and other solvents, and as a rule they can be distilled
without decomposition ; alkalies have only a partial action,
saponifying esters and forming soluble salts with phenols.

The same source may yield both a fatty and an essential oil,
e.g. the fixed and the volatile oil of almond, obtained from
bitter almonds. The fatty oil obtained by expression consists
chiefly of olein, with some palmitin, but practically no stearin,
and the marc or residue remaining is then distilled with water,
yielding the essential oil of almonds, which consists almost
entirely of benzaldehyde.

Essential oils, which are much more costly than the fixed oils,
are used in soap-making to impart a perfume to the soap.

3. The so-called **Hydrocarbon or Mineral Oils** are derived from
the Scotch paraffin shale, and American or Russian petroleum.
These oils are lighter than water, have an oily appearance,
and will give a permanent stain to paper ; they are insoluble in
water and alcohol, and can be distilled without decomposition.
They are composed only of carbon and hydrogen, hence they
are called "hydro-carbon oils". Though they are not acted
upon by alkalies, and are therefore not saponifiable, many
attempts have been made in recent years to incorporate mineral
oils in soap, generally in the form of an emulsion, which, how-

ever, soon tends .to separate on keeping, They·cannot be re-garded as soap-making materials, but find an extensive use in lubricating machinery.

II. METHODS OF MAKING SOAPS.

The methods employed in the manufacture of soap may be divided into five groups :- -

(1) Boiling the fats and alkali together under ordinary atmo-spheric pressure in open boilers, with separation of glycerine—the ordinary process of soap-boiling.

(2) Boiling the fats and alkali together under ordinary atmo-spheric pressure in open boilers, with no separation of glycerine—the ordinary process of soft-soap manufacture.

(3) Direct neutralization of fatty acids with alkali, after preliminary hydrolysis of oil or fat into fatty acids and glycerine.

(4) Mixing the fats and alkali at a temperature just sufficient to keep the fats fluid– the so-called cold process.

(5) Boiling the fats and alkali together under increased or diminished pressure in closed boilers.

The *first method* is by far the most commonly employed. In this method the fat is boiled with a solution of caustic soda, until it is saponified; then salt is added, which throws out the soap in the form of curds, which are collected and allowed to set into the form with which the public is familiar. There is also obtained what is known as "spent lye," an aqueous liquor containing the salt added, any excess of alkali that may have been used, and also the glycerine which was liberated during the process of saponification. Formerly this lye was thrown away, but now it is treated for the recovery of the glycerine it contains.

In the *second process*, the oil is boiled with caustic potash, added little by little until saponification is complete. Such soap cannot be grained out with salt, as in the first process, since sodium chloride reacts with potassium soaps, forming, by double decomposition, sodium soap and potassium chloride, as

$$C_{17}H_{15}COOK + NaCl = C_{17}H_{35}COONa + KCl$$

| potassium | sodium | sodium | potassium |
| stearate | chloride | stearate | chloride. |
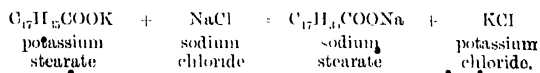
Hence the glycerine cannot be recovered from soft soaps by this means, and if it is desired to prepare soft soaps free from glycerine, as is often the case now in view of the high price attained by glycerine, the oil must first be hydrolyzed by one of the many methods available for the purpose, viz. lime saponification, Twitchell's reagent, castor-seed ferment, etc., and the separated fatty acids neutralized with caustic potash, *vide infra*.

By the *third process*, the molten fatty acids are run into the boiling alkali lye (sodium carbonate or hydroxide for hard soaps, caustic potash for soft soaps) in sufficient quantity for complete neutralization.

The *fourth* is one of the most rapid methods of soap manufacture, the fat being just melted, and then thoroughly mixed with a strong solution of caustic soda, the mixture allowed to stand for some time to allow the saponification to become complete, when the soap is ready for use. In this case, as in the preparation of soft soap, there is no salting out, and the glycerine remains in the soap.

In the *fifth method*, the fats and alkali are boiled together under increased or reduced pressure in a closed vessel or boiler, until saponification is complete, when the soap is set on one side to cool, and is then ready for sale.

The following is a general outline of the above-mentioned processes :—

1. SOAP-MAKING BY THE BOILING PROCESS, WITH SEPARATION OF GLYCERINE.

Probably 90 per cent. of the hard soap produced in this country is made by the boiling process in pans of iron, or steel-plates, and fitted with open and closed steam coils, as shown in Fig. 1.

In this method of boiling, the fat and alkali are brought together in the presence of water in such proportions as experience has shown will enable them to make soap, but the quantities are not definitely proportioned one to the other. The boiling brings about the saponification of the fats and forms the

soap, which can then be finished in any way that is desirable. There are three chief varieties of hard soap produced in this way, dependent upon certain modifications in the finishing operations; these are known as "curd," "fitted" or, in America, "settled," and "run" soaps. These, of course, are independent of varieties of soaps produced by varying the materials used.

In commencing a soap-boil it is advisable to see that the pan is quite clean; if necessary, it may be rinsed out with a little caustic soda lye. A portion of the fats to be saponified, previously melted in separate tanks, is first run in. The quantity
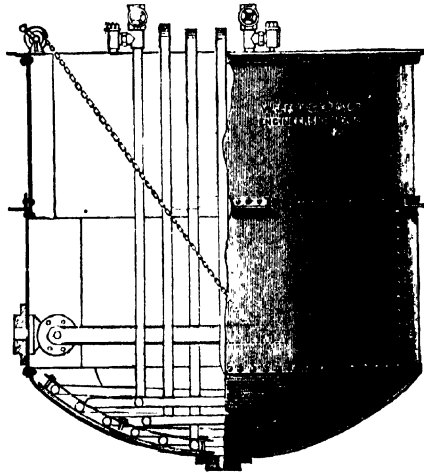
Fig. 1.—Soap-pan.

is not of much consequence, but about one-third of the total charge is a fair proportion. There is then run in soda lye at 1½ to 23°·5 Tw. (a stronger lye than this should not be used). One of the difficulties in soap-boiling is to start the saponification of the fat; if the lye be too strong, this does not take place readily enough, and other difficulties are introduced. By using weak lye, however, there is little, if any, difficulty experienced, and about 10 gallons may be allowed to every 5 cwt.

of tallow run into the pan. The steam is turned on to bring
the mass to the boil. The material may rise up in the form of
froth very considerably, this proceeding being known to soap-
makers as "fobbing". This occurs only at the beginning of a
boil or when running in more fat or alkali; if it happen, the
steam must be turned off, the mass of fob beaten down by the
hand-paddle or beater, and the pan left to itself for a few hours,
when the boiling may be resumed. It will probably be found
that the boiling will now proceed very quietly and without
further trouble, as during the time the pan has been standing
the fat and the alkali have been reacting and entering into com-
bination with one another. It is this liability to fob that renders
it undesirable that a soap-pan should be fully charged to start
with. Sometimes there is very little difficulty in starting the
saponification, at other times great difficulty is experienced.
Much will depend on the condition of the fat; if this be almost
neutral, then it will not be easy to start its saponification; on
the other hand, if it contain some free acid, this will at once
enter into combination with the alkali and form soap, which,
by increasing the emulsifying tendency of the fat, enables the
alkali and fat to more thoroughly amalgamate together, and,
therefore, facilitates the process of soap formation. With a
view of imitating this action, it is the custom of many soap-
makers, and it is a custom worth following, to throw into the pan,
on its being first charged, all the scraps of soap which they may
have about; such scraps dissolving in the weak lye, help forward
the saponification of the fat to a great extent. There are always
plenty of soap scraps about that are produced in cutting the
blocks of soap up into slabs and bars; these should always be
placed on one side, and sent into the soap-boiling house for this
particular purpose.

When the first quantities of fat and lye appear to have been
thoroughly amalgamated together, then there may be run in a
ton of oil; then—or better simultaneously—lye; this may now
be used stronger than was first employed, say 25° to 28° Tw.

The mass is now boiled up for two hours. Fobbing will
rarely occur at this stage. At the end of the time given, the

rest of the charge may be run in and the boiling continued. It is advisable to keep it well stirred, so as to bring the fat and alkali into intimate union. If the boiling be done with open steam, then the steam itself passing through the soap is almost sufficient to do this. In this case, however, there will be some considerable condensation of the steam in the pan; this must be allowed for, and rather stronger alkali, 28° to 32° Tw., employed in the last stages. If a closed steam coil be employed, then the soap must be kept stirred by means of the hand-paddle or mechanical stirrers. At the end of the boil very little stirring will be required, the soap will boil up very nicely and gently in what are known as "roses," and this gentle boil is a sign that the end is approaching. Soap-boiling is one of those processes that cannot be taught by books, owing to the difficulty of describing all the changes in appearance of a charge of soap during the process of boiling it up. The length of time a pan of soap takes to finish depends entirely on the weight of soap being treated, and may vary from five hours for a small charge, to twelve to fifteen for a large one. The end of the operation is ascertained by taking out samples from time to time by means of the paddle and examining them. It should have a firm consistency, be free from any oil or fat, and produce only a faint biting sensation on the tongue, which would show that the alkali was in slight excess, as it should be. Then again the appearance of the soap is some guide: when properly saponified it will be homogeneous and semi-transparent, look smooth and glossy, and fall off the paddle in clear flakes; on the other hand, if it be opaque and rather granular in appearance, then it is an indication that there is either an excess of fat or an excess of alkali, which will be shown by the other tests previously alluded to. Sometimes there are signs that there are free alkali and free fat present in the soap-pan at the same time, which shows that the saponification of the fat has not been properly conducted; the remedy in such a case is to add some water and proceed with the boiling.

It may be stated here that, roughly, 100 lb. of fat require 100 lb. of lye at 32° Tw. to complete saponification; cocoa-nut oil takes about one-fourth more.

Graining Out.—The next operation is that of graining out, or separating the soap from the water employed during the boiling, from the excess of alkali used, and from the glycerine liberated during the process of saponification. This may be accomplished by the addition of common salt, either dry or in solution as brine, or in the case of soaps made from cocoa-nut or palm-kernel oils, by adding caustic soda lye; either of these re-agents throws the soap out of solution in the form of grains or curds, owing to the fact that while soap is soluble in water, it is insoluble in solutions of caustic alkali or alkaline salts, and when, therefore, such are added to a solution of soap, the latter is thrown out of solution. The salt is sprinkled over the boiling soap in small quantities at a time, until the soap forms in small grains, and a quantity of lye is clearly visible when the paddle is placed in the soap and then lifted out. A very little practice soon shows the soap-maker when this point is reached. Care must, however, be taken not to add the salt in too large a quantity at a time, and to allow each portion to dissolve before adding another portion, otherwise there is a liability to get an excess of salt, and this is undesirable for two reasons: (1) because it is not economical to use more material than is necessary to do the required work; and (2) because excess of salt introduces difficulties to be overcome in subsequent operations. The soap in the pan loses its smoothness and transparency, becoming more opaque and granular; the boiling also becomes rather irregular, and tends to occur in bursts, and sometimes there is a tendency to boil over.

The solubility of a soap in salt solution varies considerably according to the fats from which it is made, tallow soap being the most easily grained, cotton-seed oil soap requiring more salt, and soaps made from cocoa-nut and palm-kernel oils requiring very large amounts of, salt to grain them thoroughly.; hence the reason for generally graining the latter soaps with caustic soda lye of $32\frac{1}{2}°$ Tw. Some soap-makers prefer to use brine at $40°$ Tw., but ordinary common salt is generally employed.

When sufficient salt or alkali has been added, and the contents of the pan separate out on the paddle into a grainy soap

and clear lye, the steam is shut off and the pan allowed to remain at rest for four or five hours, or over night, according to the size of the batch, after which the contents of the pan will have separated into two layers, the upper one consisting of soap, holding probably about 40 per cent. of water, while the lower layer is known as "spent lye" if salt has been used for graining, and as "half-spent lye" if the soap was grained with alkali.

This lye is more or less dark in colour according to the character of the fats used in making the soap, and contains in addition to the salt or alkali used for graining, sodium carbonate, any impurities which may have been present in the original caustic soda and in the fats, together with the liberated glycerine. It is drawn off, and, if spent lye, is transferred to the glycerine house with a view to the recovery of the glycerine and salt it contains; if half-spent lye, it is utilised in the pasting of fresh materials.

This concludes the first stage in the preparation of all boiled soda soaps, and it is from this point that differences of treatment arise to produce various kinds of soap. The operation of soap-boiling requires to be conducted with care and attention, and every effort should be made to see that the boiling is complete. This makes a considerable demand on the skill and experience of the soap-boiler. Too strong an alkali should not be used, for, as stated above, it would be difficult to start the saponification. Different fats will require different strengths of lye to commence saponification. Thus while tallow, palm oil, cotton-seed oil and some others will not work with lye stronger than 15° to 18° Tw., cocoa-nut oil and palm-nut oil will take lye up to 32½° Tw., saponifying best, in fact, with the strong lye. Linseed and olive oils usually work best with a lye of inter-mediate strength. Then, of course, some fats take more alkali than others, and this must be allowed for or imperfect saponification will take place. A little excess of alkali should be used, but too much must be avoided, as such excess tends to retard saponification rather than assist it.

Boiling on Strength or Clear Boiling.—After removal of the spent or half-spent lye, the soap is "closed", i.e. boiled with

sufficient water or steam to just render it smooth and homo-
geneous, and is then ready for the operation of boiling-on
strength, the object of which is to harden the soap and ensure
complete saponification. Considerable attention should be paid
to this boil, as it has a material influence on the grain and quality
of the finished soap.

Caustic soda lye at 32½° Tw. is gradually added, little by
little, with continuous boiling by means of the dry steam coil,
until a permanent strength remains, and the soap is again grained.
This operation cannot be hurried, but must take some three to five
hours, according to the size of the batch of soap being made,
and when the granular state is reached, the boiling should be
continued for a while in order to completely saponify the last
traces of neutral oil.

Steam is then shut off and the pan of soap covered up and
allowed to settle for some hours, the time varying with the size
of pan and amount of soap. At the end of this time the con-
tents of the pan will have divided into two portions; one of
soap at the top, the other of lye—"half-spent lye" it is called.
This is withdrawn and stored in a separate tank, and is used
in the first boil of a new batch of soap, as it still contains some
caustic soda. It may have a dark colour, especially if poor fats
have been used in making the soap.

Fitting. —The granular soap remaining in the pan is now
ready for the final process of "fitting", which, in the case of all
boiled soda soaps, with the exception of *Curd Soap*, follows the
operations of Pasting, Graining, and Boiling on Strength.

The soap is boiled with open steam, and water gradually
added until the soap loses its granular appearance and becomes
more transparent and homogeneous, samples being tested at
intervals as to the manner in which they drop off a hot trowel held
sideways. When the thin layer of soap slips off in two or three
flakes, and leaves the surface of the trowel clean and dry, it is
in a condition to allow the impurities to settle out of the soap
by gravitation, and after applying a good pressure of steam, so
that the contents of the pan swell as high as possible, steam is
turned off, and the pan covered, and its contents allowed to rest

for four to six days. The time required for settling depends not only on the composition of the soap, but on the size of the boil, and on the season of the year. When complete, the contents of the pan will have separated into four layers, viz. (i) on the surface, a thin crust of soap, with a small amount of fob; (ii) the good soap containing invariably 63 to 64 per cent. fatty acids; (iii) a darker, weak soap, termed "nigre", which will contain about 33 per cent. fatty acids, and (iv) a small amount of alkaline lye.

After removing the thin crust, the good soap is pumped either direct into frames (Fig. 2) (which are generally of iron, except in the case of mottled soaps, for which wooden frames are preferable), where it is allowed to solidify, or first into a crutching pan (Fig. 3), where it can be admixed with any neutralizing material, colouring matter, perfume, or other substance, and thence into the frames. After three to six days the sides and ends of the frame are removed, leaving a solid block of soap, which is

Fig. 2.—Soap frame.

then cut into slabs and bars by means of mechanical wire arrangements.
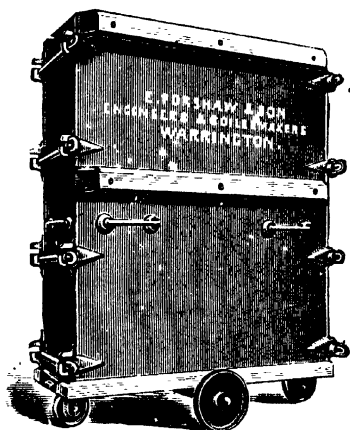
Prior to fitting, some soap-makers give the soap what is termed a "cleansing boil." This is done by closing the soap with water and steam, then adding a strong brine liquor in just sufficient amount to open the soap, and boiling with either close or open steam for three to four hours, after which the pan is allowed to settle for about twelve hours, when the soap will have separated to the top, and the brine below. The cleansing boil helps in the completion of the saponification, and therefore in the production of a more perfect soap, while it tends to wash out any excess of alkali that the curd soap may retain from

the "boiling on strength" operation, and so make a more neutral soap. Some soap-makers will, with their best qualities, give even a second cleansing boil. The brine liquor may sometimes be used more than once, according to the quality of the soap which is being made;—if from good, clean fats, the liquor may be used several times; if from poor, dirty fats, it cannot be used more than once or twice, as it becomes too highly charged with dirt to work satisfactorily. After the cleansing boil, the soap is just closed and allowed to settle as described above.
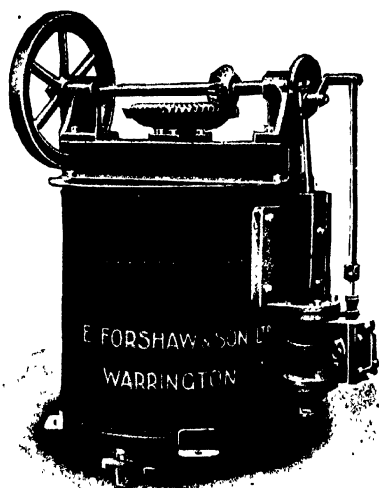
Fig. 3.—Crutching pan.

As previously mentioned, Curd Soap is not subjected to the fitting operation, but after boiling on strength, the boiling is continued until the soap is free from froth, the pan covered, and the mass allowed to rest for eight to ten hours, when the soap is ready to be run into frames, where it is crutched until perfectly smooth, and allowed to set. Curd soap is generally made from tallow, but cocoa-nut oil is sometimes blended with it.

Curd soap, while it possesses excellent detergent properties,

is apt to be rather alkaline and sharp, and therefore does not suit all purposes, but does very well as a wool-scouring soap.

Curd Mottled, or Genuine Mottled Soap, as ·distinguished from artificial mottled soaps, which are generally silicated or liquored soaps containing less than 63 per cent. fatty acids, is usually made from melted kitchen grease and bone grease, the impurities from which, remaining in the interstices of the curd, form the mottling. Its preparation is similar to that of ordinary curd soap, except that the boiling on strength operation is not continued quite so long. The soap is allowed to rest two hours, and then rapidly transferred to wooden frames.

Such is a general description of the ordinary process of soap-boiling. It is subject to a little modification here and there, according to the fancy of the soap-maker, the kind of soap being made, and the fats used.

2.—SOAP MAKING BY THE BOILING PROCESS, WITH NO SEPARATION OF GLYCERINE.

This method is employed in the manufacture of most of the soft soap produced in this country, though the direct neutralization of fatty acids with caustic potash (Process III) is now replacing it to a certain extent. Soft soap is a very important article in the textile industries, and is very extensively manufactured in some districts, though in others it is made in comparatively small quantities. The common soft soap is an amber-coloured to reddish-brown material of the consistency of butter. It is much more soluble in water than the ordinary hard soap, and usually rather more alkaline. Its detergent and scouring properties are therefore greater. While soft soap is also made, usually from cotton-seed oil and tallow, or cocoa-nut oil and tallow; it is frequently filled with starch or flour.

The alkali of soft soap is potash, although a little soda is also occasionally used in conjunction therewith; a soft soap cannot, however, be made with soda only, in the same way that hard soaps cannot be made with potash. Soft soaps owe their

consistency to the greater solubility and hygroscopic character of potash soaps.

Soft soaps are much more simply made than hard soaps. The fats and oils are boiled with the alkali till the saponification is complete ; then the soap is made, and only needs to be run into firkins or tin canisters to be ready for sale. Simple, however, as it appears in principle, soft soap is by no means easy to make. It is liable sometimes to go wrong in the boiling, and then it becomes a difficult matter to set it right.

The aim of the soft-soap maker should be to produce a clear, transparent soap, pale in colour, fairly free from odour, not too alkaline in character, and, in some cases, "figging" well. The term "figging" is applied to a peculiar star-like formation which is met with in some soft soaps, streaks of white striking inwards from the sides of the vessel holding the soap. Figging is usually considered to indicate a good quality of soft soap, but such is not really the case. A first-class soft soap can be made which will not fig, while, on the other hand, a poor soap can be produced which will fig. The figging is usually ascribed to the presence of stearate of soda in the soap, which crystallises out on the soap becoming cold, the crystals which are thereby formed giving rise to the figging. Figging is mostly met with in winter time. Unless the proportion of soda and stearic acid in the soap is very large, it does not occur in summer time.

The oils chiefly employed in making soft soaps are linseed oil, maize oil, olive oil, soya-bean oil, cotton-seed oil, whale oil, and fish oils. These form the basis of the domestic soft soaps and common industrial soft soaps. Linseed oil is the one chiefly used, as it saponifies easily and gives a good, pale-coloured transparent soap of a good consistency, fairly free from odour, and which keeps well. Whale and fish oils are largely used, being cheap; but they commonly produce dark-coloured though clear soaps. Much, however, depends on the quality of the oil which is used.

Fish-oil soaps have a fishy odour, which is not altogether objectionable. Cotton-seed, maize, and soya-bean oils make fairly good soft soaps, pale in colour and transparent, figging

well, which is not the case with linseed or fish oils. Cotton oil soaps are, however, liable to acquire a rancid odour on keeping. The quality of the cotton-seed oil has a material influence on the quality of the soap. The best refined oils produce pale-coloured, transparent soaps, the commoner grades are apt to give darker-coloured soaps, which, owing to the large proportion of stearin they contain, are liable to fig strongly. Tallow is occasionally added in making soft soaps, to cause them to fig. Olive oil soft soap is made for special purposes, such as silk-washing, etc., but olive oil, owing to its cost, is not commonly blended with other material in the manufacture of soft soap. Sometimes nut oil is added.

When white soft soaps are required, as is sometimes the case for special purposes in the cotton trade, they must be made from good white tallow, cocoa-nut oil, and perhaps a small quantity of lard or other fat which yields white soap ; particular attention must also be paid to the quality of caustic potash used, which should be of a good white colour.

The caustic potash used in making soft soap was at one time prepared by the soap-maker, for his use, by causticizing pearl-ash (carbonate of potash) with quicklime. Now, however, it is the custom for the smaller makers to purchase it from the alkali-maker, ready prepared, in iron drums, in which case it is advisable to make an examination of it, to see that it is up to full strength, of good colour, fairly free from carbonate, and does not contain much, if any, oxide of iron. Many of the lower grades of caustic potash which are produced are defective in one or other of these points. It is very important that the caustic potash lye should contain carbonates, which promotes brightness and helps to give transparency to the soap. If the caustic potash is deficient in carbonate this may be added in the form of a solution of refined pearl-ash, to the extent of about 5 per cent. Too much must not be added, or the soap will become thin, and a whiteness will form on it.

It is advisable that the soap-maker should prepare at least two potash lyes of different strengths, one of 23° Tw. and one of 40° Tw. Some makers provide lye of three strengths—

14° Tw., 23° Tw., and 40° Tw.   Much, of course, depends on
the construction of the pan in which the soft soap is being
made. If the pan be one which is heated by fire only then a
weak lye of 14° Tw. may be used with advantage, while if it
is fitted for steam-heating with open or closed coils, then
strong lye may be used, say 23° Tw.   In the first case, of course,
as the boiling proceeds the lye gets stronger, while when work-
ing with the open steam the tendency is for it to get weaker.
.It is by far the best plan to make the soap in pans fitted with
open and close steam coils.

In making soft soap, about one half of the full charge of oil
is run into the pan and heated by means of the closed steam
coil, a quantity of lye at 23° Tw., equal in volume to the oil,
being then run in and open steam applied.

The lye should be run in slowly, and the mixing of the lye
and oil carefully watched.   Presently the oil will commence to
saponify, when it must be well stirred, for it will begin to swell
and rise in the pan.   As soon as this is seen, more lye, equal to
the first quantity in volume, may be run in and the boiling con-
tinued.   Two things may take place in the early stages of saponi-
fication,—the oil and lye may boil over, or they may set into a
stiff pasty mass.   In either case trouble may be looked for.
The remedy in the first case is to turn off steam and beat down
the bubbling soap with the paddle; that in the second case
consists in adding more lye and water, in boiling up, stirring
well, and breaking up the mass as much as possible, but the
process becomes tedious because it is difficult to break up the
masses of soap, and they are not easily dissolved in the boiling soap
in which they float.   These troubles will be avoided if a quantity
of finished soap be left in the pan from a preceding operation.

When the oil and lye have amalgamated, then the rest of
the charge of oil may be run in and the further quantity of
alkali at 40° Tw. may be added.   It may be mentioned here
that, as a rule, 100lb. of oil requires about 100lb. of caustic
potash lye at 40° Tw. to saponify it, so that the soap-maker
may base his calculations as to the quantity of alkali required
on these data.

The soap is now boiled either by fire heat or preferably by the closed steam coil. Generally it is not necessary to stir it, as the boiling keeps it in continual agitation; it is a good plan now and again to send a sharp current of open steam through it, or to stir it up with an iron paddle, taking special note of any hard lumps of soap that may settle down at the bottom of the pan.

After a time the saponification of the oil will be complete, and the soap formed. To ascertain this, take out a sample of the soap with a spatula, place it on a piece of glass, and allow it to cool, when one of three things will be observed :—

1. The soap may be clear and translucent, which indicates that the soap is properly formed and only needs boiling down to the proper strength.

2. The spot of cold soap has a fatty border. In this case more lye is required, and the soap-boiler should add some of either 23° Tw., or even as strong as 38° Tw., and boil up a little longer, when another sample may be drawn to see how the soap is progressing.

3. The spot of soap is of a grey colour, lustreless, and somewhat granular in appearance. In this case too much lye has been added, and to remedy this a quantity of oil which has been mixed with a weak lye should be added, and the soap boiled up further. The experienced soap-maker can tell by the manner of the soap boiling how it is progressing, and whether it wants more lye or oil.

The boiling should go on quietly, free from any jumping or bumping. The boiling down is carried on until a sample taken out and cooled on a glass plate shows the proper consistency and brightness of appearance.

It should be short in texture, and not draw out in threads, which indicates an excess of water.

When finished, the soap is run into the firkins or other packages to cool, and is then ready for sale.

Linseed oil yields a soap of a dark amber colour, with a pleasant odour.

Whale oil yields a dark reddish soap, varying somewhat in colour according to the quality of the oil used; but always

having a fishy smell, Fish oils may be used with a similar result.

Cotton-seed oil yields a soap varying from golden to an amber colour, according to the degree of refinement of the oil. Freshly made cotton-oil soaps are free from odour, but on being kept are rather apt to become rancid and develop an odour.

Olive oil yields a fine soap, varying from amber to greenish in hue, according to the grade of the oil used. Lard gives a fine white soap, not so stiff as a tallow soap. Hemp-seed oil gives a green-coloured soap. Cocoa-nut oil gives a fine white soap. Tallow gives a stiff soap, apt to fig somewhat.

The colour of the finished soap depends largely on the care and attention given to it during the process of manufacture, and also on the method of heating the soap-pan. A fire-heated pan undoubtedly produces a darker soap than a steam-heated pan, so that the latter form of pan is much to be preferred.

Sometimes figging is brought about by using a little soda along with the potash, as, for instance, in the following recipe : —1000 lb. of oil is boiled with 535 lb. caustic potash lye at 32° Tw., to start the saponification ; then there is added 150 lb. potash lye at 42° Tw., and 470 lb. caustic soda lye at 32° Tw. The proportion of sodium hydroxide should not exceed 20 per cent. on the fat stock.

The finished soft soap is usually from $2\frac{1}{4}$ to $2\frac{1}{2}$ times the weight of the oil used, the yield being less the more caustic soda is employed. Good soft soap should contain 42·5 per cent. of fat, with 10 per cent. of potash, and 47·5 per cent. of water; some samples have as low as 40 per cent. of fat, while others have as much as 50 per cent. of fat.

Rosin makes a good cheapening agent for soft soaps up to 10 to 14 per cent. of stock, increasing their solubility, and hence their lathering properties. The rosin may be melted in the other oils prior to saponification, and run in with them into the pan. Some makers employ soda to convert the rosin into soap before mixing it with the other ingredients, in which case $2\frac{3}{4}$ cwt. of soda ash (58°) is dissolved in four times its weight of water in a steam-jacketed pan, and 18 cwt. of rosin broken into

small pieces added.   The whole is heated by means of the
open steam coil, taking care to prevent boiling over.   When
all effervescence has ceased the soap is run into the pan of soft
soap.

The cheaper grades of rosin produce darkish coloured soap,
so that if the colour of the finished soap be a matter of import-
ance, the better qualities of rosin must be used, or it may be
purified by the following process : The rosin is saponified with
soda-ash, as described above, then the rosin soap is salted out
by the addition of ordinary salt, and time allowed for the soap
to settle out.   Then the lye is run off, and with it a large pro-
portion of the colouring matter of the rosin.   The rosin soap
thus purified may be added to the soft soap.

3. DIRECT NEUTRALIZATION OF FATTY ACIDS WITH ALKALI.

This process is becoming increasingly popular, owing both
to improved methods for the preliminary separation of fatty
acids from glycerine, and to the increased value of the latter
body, the glycerine separated by Twitchell's reagent and the
castor-seed ferment process being more easily recovered than
soap lye glycerine.   Unfortunately no method has yet been de-
vised which will completely hydrolyze an oil, otherwise the pro-
cess would be one of the simplest means of manufacturing soap.

In the case of hard soaps, sodium carbonate, which is much
cheaper than caustic soda, can be employed for the saponifica-
tion.   This may be carried out in an open pan fitted with an
open steam coil, or a removable stirrer, soda ash ($58°$) to the
extent of 19 per cent. of the fatty acids to be saponified, being
dissolved in water by means of steam until a density of $53°$ Tw.
is attained, when the molten fatty acids are gradually added, the
mass being gently boiled all the time.   The fatty acids must
not be added too rapidly or the boiling be too vigorous, or the
contents of the pan will boil over.   This may be checked by
agitation or stopping the flow of fatty acids.   A more satis-
factory method is to dissolve half the quantity of soda ash in
water to a solution of $64°$ Tw. density, run the fatty acids
into this with continuous boiling, until all the alkali has been

neutralized, and then add alternately fatty acids and soda ash, sprinkling the latter in the dry state over the pan, until all has been added. Since, as mentioned above, fatty acids free from unhydrolyzed glycerides are not commercially obtainable, and the glycerides can only be saponified by means of caustic alkali, when all the sodium carbonate has been neutralized, caustic lye at $32\frac{1}{2}°$ Tw. is gradually added, and the operations of boiling on strength and fitting carried out in exactly the same way as described under the Boiling Process, pp. 13-14.

If desired, the fatty acids may be saponified with caustic soda by running them into the requisite quantity (about 14·2 per cent.) dissolved in water in the pan to a density of $32\frac{1}{2}°$ Tw., boiling steadily all the time.

For the production of soft soap from fatty acids, the procedure is very similar to the above, the pan being charged with a mixture of caustic potash lye and caustic soda lye, in the desired proportions, at a density of 53° Tw., and the molten fatty acids added to the boiling lye. The soap is tested on a glass plate, as already described under Process II, p. 21, to determine when the fatty acids and alkali are in the right proportion, and the boiling continued until the soap is no longer stringy. By this process, soft soap can easily be made in two or three hours.

If rosin is to be used in these soaps, it may be melted in the hot fatty acids, and run in with them into the alkali lye.

4. THE COLD PROCESS OF SOAP-MAKING.

This is the simplest and most rapid method of making hard soap, and requires very little plant or labour, while a further advantage is that the manufacture of soap by this process is not *soap-boiling*, and therefore does not come under the designation "Offensive Trade".

Small quantities can be made by its means, which is not the case with the boiling process, and the yield of soap from any given weight of fat is larger on account of the fact that all the material used in making the soap remains therein.

The disadvantage of the cold-process is that it is difficult, indeed impossible, to secure complete saponification of the whole

of the fat used, without having a considerable excess of alkali. There is consequently always present in these soaps a small but variable quantity of free fat. Then they also contain a little free alkali, which causes the soap to have an irritating effect on many skins. The presence of the free fat may sometimes lead to the soap becoming rancid. Cold-process soaps, when exposed to the air, are rather liable to sweat, and they dry up more easily than a boiled soap, so that they do not, look well when old. They dissolve, however, more freely in water, and therefore lather better; for hard waters they are better suited than a boiled soap.

As all the ingredients which are used remain in the soap, it is evident that all the materials used must be of the best quality if a good grade of soap is to be made.

The fat most used and best adapted for making soap by this process is cocoa-nut oil; at one time it was considered that a cold-process soap could not be made without this oil forming fully one-half of the fats used. This, however, was at the time when highly causticized lyes were not made, and when caustics of high strength were unknown. Now, however, any kind of fat may be employed; but still cocoa-nut oil remains the chief fat employed. Its merit lies in the fact that it saponifies more readily with strong alkalies, such as have to be used, than any other fat. It yields a soap of a fine colour, which dissolves easily in cold water, and lathers very freely; on the other hand, it is apt to be harsh and to have an irritating effect on delicate skins. Tallow is also very largely used for cold-process soaps, giving good white soaps of a firm texture, durable in use. Palm oil, cotton-seed oil, and castor oil, are also frequently employed. The soap-maker, indeed, may use any fat or admixture of fats according to the quality and kind of soap he desires to produce.

Whatever fats are used, they should be of good quality, free from any foreign matter, and quite fresh. It is advisable to subject them to a clarifying process before using them; this process may take the form of melting and allowing to settle, or the fat may be melted over a salt lye of about 10° Tw., in each case using only the clear fat which rises to the top. It is of

great importance to use fresh fats and fats free from any con-
siderable proportion of free fatty acids, as the latter tend to the
formation of soap which is not uniform in grain; the free fatty
acids, when the alkali is mixed with the fat, immediately com-
bine with it to form soap, which separates from the rest of
the mass in the form of grains and curds, and, as the temper-
ature of the soap is never raised sufficiently high to dissolve
these in the rest of the soap, the finished product is gritty in
use. Such soap also encloses particles of free fat and alkali,
giving rise to what is technically termed "bunching". If it
be suspected that any particular batch of fat contains too much
free fatty acid, this may be removed by heating the fat to just
above its melting-point, then thoroughly mixing it with a little
weak lye made from soda ash of about 2° to 3° Tw.; the alkali
takes out the acid in the form of soap, which dissolves in the
lye. By keeping the mass at 130° to 150° F., the purified fat
will rise to the top, and may be skimmed off and used. If any
difficulty be experienced in separating the clear fat, a little salt
brine added will remove it. It pays best to use only the best
grades of fat.

The alkali used must be the highest grade of caustic that can
be bought, either the 77 per cent. solid caustic soda or the 100° Tw.
liquid caustic soda. The strength of lye most commonly used
is 70° to 72° Tw., containing 32 to 33 per cent. of actual caustic
soda. The alkaline lye should be made with the softest water
obtainable. Low grades of caustic are not suitable for making
soap by the cold process, inasmuch as the foreign salts and im-
purities they contain interfere with the complete saponification
of the fat, and lead to the production of a soap which contains a
larger proportion of free fat and free alkali. Then, again, if a
very low grade of caustic were used, the impurities and salts
would be liable to cause efflorescence on the surface, and spoil
the appearance of the soap and of any wrappers in which it
might be placed.

As regards the quantity of lye used and the proper strengths
at which to use it, these necessarily vary with the kind of fat
employed.. Cocoa-nut oil, for instance, will require more lye,

and a stronger . one may be used than is the case with tallow.

It has been found that cocoa-nut oil and cotton oil saponify best with a lye of 72° Tw., while for tallow, palm oil, and most other fats the saponification proceeds best at 66° Tw. Too strong a lye should be avoided, as then the soap is made rather curdy in texture and the saponification is imperfect, the soap being hard and rough. It is better to use a lye one or two degrees weaker than stronger.

As regards the quantity of lye to be used, cocoa-nut oil, as before mentioned, takes the most, 100 lb. of the oil taking 50 lb. of lye at 72° Tw. made from 77 per cent. caustic soda. If a lower grade of caustic, say 70 per cent., be used, then the lye may be made stronger, say 77° Tw., and the same quantity employed.

Tallow, cotton oil, palm oil, and other fats do not require so much alkali; in their case it is best to use a lye of 66° Tw., and of this 50 lb. will be required for each 100 lb. of fat.

Using the fats and oils and lye in the proportions and strengths given, the finished soaps will contain about 25 per cent. of water, which is a fair average quantity. If a soap containing more water be desired, then a weaker lye may be used, while if a stronger soap is wanted, then a stronger lye must be employed.

It may again be stated that in the cold process the saponification is never complete; there is always in the finished soap a little free fat and a little free alkali. In making a toilet soap it is advisable to· so proportion the fats and alkalies and the strength of the lye used as to leave as little free alkali as possible.

Having so far dealt with the materials and principles of the cold process of soap-making, we may now proceed to describe in detail the operation itself.

Working of the Cold Process.—The fats and oils which are to be used are placed in a pan which ought to be fitted with a mixing arrangement, and either steam jacketed or containing steam coils. The fats are just melted, the temperature being raised only slightly above that necessary to keep them fluid. When cocoa-nut oil is used it should be about 80° F. in the summer

and 90° to 95° F. in the winter; with a mixture of cocoa-nut
oil and tallow about 100° F. in the summer, and 120° F.* in
the winter; with tallow and palm oil from 110° to 120° F. in
summer, and about 130° F. in winter.   When melted, lye is
run in with constant stirring, which is continued until the mass
of fat and lye begins to thicken and flow from a paddle in a uni-
form sluggish stream.   The temperature of the lye may be that
of an average summer heat, 70° to 80° F.   There is no need to
heat or warm it in summer, but in winter it may be advisable
to heat the lye to 80° F. before mixing it with the oil.   After the
lye and oil have been mixed and it begins to thicken, the soap
mass is run into the frames, which are then covered over with
sacking to keep the heat in as much as possible, and left for from
three days to a week for the soap to fully form, after which it
may be cut up in the usual way.

Although comparatively simple, yet, as with all processes of
soap-making, the cold process must be conducted with care and
attention to some points of detail, or otherwise the product will
not be quite right.   Certain of these points have already been
mentioned, and others may now be briefly referred to.   To ensure
a perfectly good product, the fats must be of good quality and
without free fatty acids, or the soap will be liable to turn out
curdy, and not homogeneous, in structure.

The fats should be at the right temperature—not too cold,
or otherwise they might set on adding the lye; and not too hot,
or then the saponification of portions may take place too rapidly
and a curdy or grainy soap be produced.   The strength of the
lye has already been dealt with, and does not need repeating
here.   The mixing or crutching of the fat and lye together
should be thorough, but not too prolonged; or there is a tendency
for the materials to separate out in the frames, and an indifferent
quality of soap is produced.   In that case only one thing can be
done, and that is, to throw the materials into the soapboiler and
boil them up.

The frames into which the soap is run from the crutchers
should not be too large—those holding from 2 to 2½ cwt. are
best,—and it is preferable that these should be low and broad

rather than narrow and high. The latter shape of frames retains the heat too long, and the soap does not set properly, while with the low flat frames covered with sacking the heat is retained sufficiently long to ensure the proper saponification taking place. Too much heat should be avoided, as then there is a risk of oil separating out. In the summer-time this is a risk specially to be guarded against.

Hard White Soap.—(1) 100 lb. good white tallow, 50 lb. caustic soda lye at 68° Tw.

Hard White Soap.—(2) 100 lb. cocoa-nut oil, 50 lb. caustic soda lye at 72° Tw.

Hard Yellow Soap.—50 lb. cocoa-nut oil, 30 lb. tallow, 20. lb. palm oil, 25 lb. castor oil, 63 lb. caustic soda lye at 70° Tw.

Pale Soap.—30 lb. cocoa-nut oil, 25 lb. tallow, 25 lb. palm oil, 25 lb. castor oil, 63 lb. caustic soda lye at 70° Tw.

The replacement of a portion of the soda lye, say one-fourth, by caustic potash of the same strength, much improves both the appearance and quality of these soaps. Soap-makers working from the above recipes can easily reckon out the respective quantities of soda and potash.

5. BOILING THE FATS AND ALKALIES TOGETHER UNDER IN-
   CREASED OR DIMINISHED PRESSURE IN CLOSED BOILERS.

During recent years attempts have been made to accelerate the saponification process by heating the fats and alkalies, in the correct proportions, as given under the Cold Process, in steam-jacketed vessels, either under increased pressure or *in vacuo*, but the processes have not so far been very extensively adopted.

W. J. Fraser & Co. make a high-pressure soapboiler, which is shown in Fig. 4. This boiler, practically an autoclave, is 4 feet in diameter and 8 feet high, and is made of steel boiler plate, and is fitted with steel manhole and cover. The fittings usually attached are—charging pipe and valve, outlet pipe and valve, shown at the bottom of the illustration, thermometer tube and thermometer, a safety valve, which is usually set to

blow off at 65 lb. to 7C lb. pressure. The boiler is set in a brick-work fireplace, the fire play-ing on the bottom and a por-tion of the side. The brackets which are fitted on the side of the boiler are for supporting it on the brickwork.

These pans are worked by putting in the charge of fat, the right quantity of alkali and water, then heating and maintaining the pressure at 60 lb. to 65 lb. for about four to five hours, when, as a rule, the saponification will be com-plete. The soap may next be run off into crutchers, and scent, etc., mixed with it, and then it is framed. The pan is ready for a new charge, which is run in immediately the old one is discharged. Two batches of soap may thus be made in one pan in the course of a day. The weight of the charge is 1 ton.

FIG. 4.—High-pressure Soapboiler.

The soap, as made in this manner, contains the whole of the ingredients added; there is no salting out, nor any lyes to run away. A great deal of the success of making soap by this high-pressure system depends upon employing the right proportion of alkali to fat and the proper quantity of water, as, if too much be used, the soap comes out too soft.

An analysis of a sample of soap made by the high-pressure system, by the author, showed it to contain—

20·79 per cent. of water.
7·61 per cent. of combined soda (Na_2O).
0·28 per cent. of free alkali (Na_2O).
66·12 per cent. of fatty anhydrides.
)·20 per cent. of free fat.
i·CO per cent. of glycerine, saline bodies.

The sample was firm and of excellent quality, which shows

that the high-pressure system can make as good soap as the low-pressure system commonly in use, while a larger quantity of soap can be turned out in a given time.

III. SPECIAL TEXTILE SOAPS.

There are three distinct branches of the textile industry in which considerable quantities of soap are consumed, viz. the wool industry, the silk industry, and the cotton and linen industry. In the two first-mentioned the fibres dealt with are of animal origin, and are of complex composition, being associated with a large amount of impurities, which in the case of wool ranges from 20 to 50 per cent., or even higher, and with silk, from 20 to 30 per cent. The cotton and linen industry, on the other hand, employs vegetable fibres, which consist of nearly pure cellulose, containing only about 5 per cent. of non-cellulose substances.

All soaps used for textile purposes must fulfil two requirements; they must not contain anything which will injure the fibres, and they must not deposit any substance on the fibres which will interfere with the subsequent dyeing and other operations.

Since wool contains such a large amount of impurity, more soap is used in this than in the other two industries, and this may therefore be considered first.

(a) Wool Soaps.

The wool fibre is very sensitive to the action of caustic alkali, both concentrated and dilute solutions tending to dissolve it. The presence of caustic alkali, therefore, even in small amount, is very objectionable in any soap intended for wool-washing, causing the fibre to lose its lustre and acquire a harsh feel. Sodium carbonate in dilute solution is, however, less harmful, and potassium carbonate still less so.

In the woollen trades soap is used in at least three distinct stages of the manufacture, viz. :—

1. Scouring raw wool.
2. Scouring wool yarns and cloths.
3. Milling or fulling woollen cloths.

(1) **Scouring Raw Wool.**—The wool on the sheep's back is very greasy and dirty, the wool fibres being encrusted with wool-fat and wool-perspiration (exuded from the skin of the sheep), which consist of cholesterol and isocholesterol, potassium salts of fatty acids, and small quantities of chloride. sulphate, and phosphate of potash. The object of the scouring operation is the complete removal of these substances, which prevent the satisfactory dyeing, carding, spinning, weaving, and finishing of the wool. The method of treatment depends on the quality of the wool.

The best soap for scouring wool is one that is neutral, contains no free caustic alkali or unsaponified fat, is free from rosin, mineral oil, or appreciable quantity of unsaponifiable matter, or from filling of any kind. For the finest wool a neutral potash-olive oil soap should be used, as, owing to its ready solubility in water, it quickly penetrates the fibres, and is easily washed out, producing a good "feel," and tending to preserve the lustre and pliability of the fibre.

With lower classes of wool, for which the high price of olive-oil soap renders it unsuitable, excellent results may be obtained by the use of curd mottled or ordinary curd soap, free from uncombined caustic alkali, but containing a small amount of carbonated alkali. A little sodium carbonate may even be added to the bath, while in the case of the lowest grades of wool some scourers use a dilute solution of sodium carbonate or sesquicarbonate only.

As to the action of soap, its general application for washing and scouring purposes is undoubtedly due to its property of easily penetrating within the fibre and coming into intimate contact with the fibre, of easily removing the fat by emulsifying it, and consequently giving the water a chance of washing it off the fibre. The old view, due to Chevreul, that soap was decomposed by cold water into free caustic alkali and an acid salt, which latter is deposited on the fibre, preventing the dirt from settling down again on it, attributed the scouring, washing, and emulsifying property of soap to the dilute solution of the caustic alkali. This view, however, was an erroneous one, since a very

dilute solution of caustic alkali could not replace soap, and for the further reason that a hot and clear soap solution (when no hydrolytic action has taken place to all appearances) cleanses far better than a cold one.

Many other theories have been advanced to explain the detergent action of soap, one of the most recent investigators of the subject being Hillyer ("Journ. Amer. Chem. Soc.," 1903, 524), who concludes that the cleansing action of soap is chiefly due to its power of emulsifying oily substances, and of wetting and penetrating into greasy surfaces.

The following are typical analyses of grey mottled soap, which is usually made from bone fat or kitchen grease, and cotton oil or cocoa-nut oil :—

	Per cent.	Per cent.
Moisture	29·83	25·67
Fatty Anhydrides	60·93	63·31
Free caustic alkali	nil	nil
Carbonated alkali, as Na_2O . . .	0·25	0·28
Combined alkali, as Na_2O . . .	7·17	7·78
Unsaponifiable matter	0·39	0·32
Titre	39·3° C	38·7° C.

Cotton-seed oil soaps are also much used; these are imported from America, and are cheap, and are found fairly efficient, Such a soap contains :—

	Per cent.
Fatty anhydrides	61·97
Free fat	0·67
Combined alkali, as Na_2O . . .	7·18
Free alkali, as Na_2O	0·35
Water	28·94
Salts	0·89

French and Italian made green olive-oil soaps are also used. These soaps are sold as containing 62 per cent. of fatty matter. An analysis of two samples of this kind of soap showed them to contain :—

	Per cent.	Per cent.
Combined fat	59·90	63·74
Free fat	0·36	1·01
Combined alkali, as Na_2O . . .	7·00	7·25
Free alkali, as Na_2O . . .	0·34	0·81
Water	32·16	25·58
Salts	0·24	...

These olive-oil soaps work well, although they are somewhat expensive.

Soft soaps are more expensive than hard soaps on account of having to be made with caustic potash, but they agree well with the wool fibre. Such soaps made from olive oil, cotton oil, or lard oil, give very good results. A good, well-made soft soap will contain :—

						Per cent.
Fatty matter	.	.	.	.	.	44·0
Combined alkali, as K_2O	.	.	.	.	.	8·2
Free alkali, as K_2O	.	.	.	.	.	0·5
Water and glycerine .	.	.	.	.	.	47·3

The reason why soft soaps suit wool better, leaving it with a softer feel and a more silky lustre than hard soaps do, has not yet been definitely settled. Some authorities are inclined to think the glycerine which many soft soaps contain has some influence, but that is doubtful, for the quantity, only about 4 per cent., seems too small to exert any marked effect.

It is worth bearing in mind that raw wool contains naturally some soap, and that the wool fat possesses considerable emulsifying properties, thus making it easy to remove from the fibre. The following analysis of raw wool will give some idea of its composition :—

							Per cent.
Water	.	.	.	.	.	.	23·48
Soap matter	.	.	.	.	.	.	21·13
Wool fat .	.	.	.	.	.	.	9·26
Wool fibre	.	.	.	.	.	.	43·20
Dirt .	.	.	.	.	.	.	2·93

The soap matter is sometimes called wool perspiration, suint, or yolk, and is soluble in water.

The wool fat consists largely of a neutral and unsaponifiable substance known as cholesterol, to the extent of perhaps 7 per cent. of the raw wool, the rest being saponifiable fats (see p. 49).

One feature of wool fat is that it is capable of mechanically combining with water. It forms then the substance known as lanolin.

(2) **Wool, Yarn, and Cloth-Scouring Soaps.**—After being cleansed from the grease and dirt it contains, wool is oiled pre-

paratory to spinning (see "Wool Oils"), and when spun into yarn and woven into cloth, this oil must be removed. This is generally effected by boiling in alkaline solutions with or without soap. Such soaps may be the same as those already described as being used in wool-washing. Really, much would depend on the character of the oil used on the wool. If this be of an acid character, being composed wholly or partially of oleic acid, then the soap may contain an excess of free alkali, either in the form of caustic soda or carbonate of soda, for this excess would be practically neutralized at once when in use, by the oleic acid.

The soap most commonly employed for this purpose is that made from oleine (so-called red oil) and caustic soda ; for lower grade materials an inferior curd, generally termed "second curd" is often used, whilst for the cheapest qualities a soap containing a small proportion of rosin may be employed.

The soap may also be supplemented in the scouring liquors by the use of sodium carbonate. When the oil consists chiefly of a fatty oil it will be found best to use a neutral soap, and to depend largely on the emulsifying properties of this soap. Soft soaps are here most serviceable, and the addition of a little caustic potash would facilitate the extraction of the oil.

A special soap emulsion for wool-washing, patented by Crefelde Seifenfabrik Stockhausen und Traiser (Fr. Patent, 396493, 1908) consists of 1 part of the sodium soap made from a sulphated fat or oil, or sulphated oleic acid, dissolved in 1·5 parts of water, and thoroughly emulsified with 1 to 2 parts of tetrachlorethane, pentachlorethane, trichlorethylene, or tetrachlorethylene.

(3). **Wool-milling Soaps.** — Lastly, soaps are used in the milling or fulling of woollen cloths after dyeing. The soap used for this purpose should be one that is easily soluble in water, and should contain no free alkali or free fat. The freedom from alkali is necessary in order to secure that the colour of the dyed goods should not undergo any material change of tone or be caused to run, which might happen if the soap were alkaline in character, and, further, that the wool fibre be left soft and supple, and firm in feel. The best soap for this

purpose is soft soap, thoroughly well made from olive oil. Tallow and palm-oil soaps, while good in some respects, are not sufficiently soluble to be useful alone. Cocoa-nut and palm-kernel oils make good white soaps, which are more freely soluble in water than other soaps, and suit industrial waters much better. They are apt to turn slightly rancid. These oils are much used in conjunction with tallow in making white curd soaps, the addition of oil making the tallow soap much more readily soluble. Cotton-seed oil soap has often a disagreeable smell, which develops on standing. Also, unless made from well-refined oil, it is apt to contain colouring matters and resinifying bodies which tend to impart yellow stains to cloth.

It has been proposed to use, as a substitute for the ordinary soaps in the milling of woollen goods, a preparation analogous to Turkey-red oil obtained in the following manner. To a quantity of commercial oleic acid (oleine), contained in a high cask, concentrated sulphuric acid (66° B.) is added, in small portions at a time, during ten to twelve hours, the mixture being well agitated and the temperature kept below 40° C. until the dark brown, viscous liquid, when shaken up with cold water in a test-tube, gives a clear solution, which on standing may develop a slight turbidity, but must not separate out any layer of oil. The contents of the cask are then run off into another vessel with an inclined bottom, containing a concentrated solution of Glauber's salt, well mixed, and then allowed to stand for twenty-four hours.

The salt solution is run from below the oily layer, and after again standing and separating from the small amount of oil, it may be employed in dyeing, as a Glauber's salt and sulphuric acid solution.

The oil, "sulpho-oleic acid," is now ready for use. Its characteristic properties are, solubility in water, and its acid reaction.

The strongly acid reaction may be corrected by partial neutralization with alkalis, while for milling goods dyed with the woods, indigo or alizarine, the sulphated oleïne is exactly neutralized in dilute solution with soda or ammonia.

The sulphated oil will mix with other soaps, but, being acid, it of course liberates their fatty acids.

Although the preparation of this sulphated oleine is somewhat more complicated than that of ordinary soap, the advantages which it presents over ordinary soap in its solubility in both acid and alkaline solution and in water, and the other properties described, more than compensate for the additional trouble; also, less of it is required.

A somewhat similar preparation is a saponified Turkey-red oil, which is sold under the name of *Isosoap*. This is a rather sticky, solid soap, containing about 70 per cent. of total fatty matter and about 2 per cent. of neutral fat. It is readily soluble in water, forming a clear solution which remains bright even when cold. The addition of an organic acid, such as acetic acid, to a 2 to 3 per cent. solution of the soap does not decompose it, and no insoluble soaps are precipitated when solutions containing small quantities of soluble calcium or magnesium salts are added, indeed the isosoap solution is claimed to redissolve any lime soap formed by the use of other soaps. In addition to this useful property, it very readily emulsifies with oils, so that it forms a valuable adjunct to the ordinary soap-baths, its use during scouring and milling wool distinctly improving its texture.

(b) SILK SOAPS.

In the manufacture of silk goods there are two purposes for which soap is used :—

1. Degumming.
2. During and after dyeing.

(1) **Degumming.**—Soap has been used from very early times in the process of boiling off or degumming silk. The silk fibre, as it is spun by the silkworm, is a long, cylindrical fibre formed of two portions—an inner portion, or the silk fibre proper, named "fibroin," and an outer portion, constituting 20 to 30 per cent. of the total fibre, called the "gum" or "glue,"—technically "sericin". The fibroin is a lustrous, soft fibre, but the coating of sericin dulls this lustre and imparts a harsh feel. To obtain,

therefore, the full lustre of the silk, the outer coating of sericin, or gum, must be removed, and this is universally effected by two or three successive boilings in a solution of soap. Generally the first operation is carried on at a temperature of 190° to 200° F.; there is used about 3 lb. of soap to 10 lb. of silk, with 25 to 30 gallons of water. This liquor causes the silk to swell up, then the gum begins to dissolve away. This first operation is generally known as "stripping," or by the French term "*de gommage*". The second operation consists in using a weaker soap liquor, 1 lb. in 30 gallons of water to each 10 lb. of silk, and at from 200° to 210° F. It is called "boiling off"; the whole of the gum is removed, leaving the silk quite clean, lustrous, and supple. The used soap liquor is known as "boiled-off liquor," and is used in the dyeing of the silk.

Soap to be suitable for boiling off silk should be easily soluble in water, for fluidity means easy penetration into the substance of the silk fabric, and also easier washing out of the silk afterwards. Further, it should be free from colour, so that it will not lead to the silk becoming stained, and it should not be liable to become rancid, and so impart an unpleasant odour to the silk.

It is not necessary that the soap should be quite neutral; a slight degree of alkalinity is rather an advantage, for the silk gum is rather more soluble in alkaline solutions than in neutral solutions; but an excess of free alkali in the soap must be avoided, particularly if that free alkali is present in the form of caustic soda, for this may affect the fibroin of the silk, making it hard and dull.

The best soap for silk is a soft soap made from good olive oil or arachis oil, for such soaps are easily soluble and pleasant in odour. Hard soaps made from the same oils, particularly olive-oil soap, are generally used, as they are cheaper than soft soap. Bleached palm-oil soap, either hard or soft, does well, but is not so soluble as an olive-oil soap. Lard-oil soap is frequently used for the purpose in America.

Tallow soaps are too slowly soluble to be suitable, and should never be used. Cotton-oil soaps are apt to be coloured, and

also go rancid. Palm-nut oil and cocoa-nut oil soaps are excellent as regards being soluble and free from colour, but they have a tendency to become rancid, which is rather objectionable. Soaps made from oleic acid are very good, being easily soluble and free from odour.

Should the silkworker prefer to use an alkaline soap, it is better to buy a neutral soap from the soap manufacturer and add a little potassium carbonate (pearl-ash) himself, as he will then know what he is working with. The use and treatment of the old soap or boiled-off liquors will be dealt with later on.

Calliat has patented (Fr. Pt. 426065, 1910) a special liquid soap for boiling off silk, consisting of 100 parts of oleic acid dissolved in 40 parts of methylated spirit, and saponified in the cold with 40 parts of alkaline lye at 57° Tw.

(2) **During and After Dyeing.**—Soap is frequently used in the dyeing of silk, sometimes by itself, but more often in conjunction with acetic or sulphuric acid. Any good, well-made soap will answer for this purpose ; one of the chief requirements is that the soap shall be made from fats that will not become rancid, for the silk takes up a great deal of the soap liquor, and if acid has been used in the bath, the fatty matter of the soap is present largely in the free or acid condition, and it is difficult to eliminate this from the silk. The writer has handled dyed silks which had a strong odour due to the use of soap made from fats that have turned rancid. A good olive-oil or palm-oil soap is very good for dyeing silk, or an oleic acid soap may be used. Rosin must on no account be present in soap employed at this stage.

(c) SOAPS FOR COTTON GOODS.

As already mentioned, the vegetable fibres employed in the manufacture of cotton and linen goods contain very much less impurity than the wool and silk fibres, and consequently the amount of soap used in this industry is much less, being applied only to the fabric. It is employed in three different operations :—

1. Cleansing the cotton goods preparatory to dyeing.

2. During and after dyeing.

3. ·In calico printing.

(1) **Cleansing Raw Cotton Goods.**—Since dilute caustic alkali has no harmful action upon the cotton fibre, the soap used in cleansing and preparing cotton goods for dyeing need not be neutral; in fact, slight alkalinity assists the cleansing. Any curd soap made from tallow, or tallow with a small proportion of cocoa-nut oil, may be used for the purpose.

(2) **Dyers' Soaps.**—Soap is used to a fairly considerable extent in the dyeing of cotton goods. In the dyeing of many direct colours, like Congo-red, benzopurpurine, etc., soap is frequently used to the extent of 3 to $3\frac{1}{2}$ lb. per cwt. of cotton which is dyed. Almost any good, well-made soap will answer here.

The Turkey-red, alizarine-red, and Para-red dyer uses soap after dyeing his cotton goods. The object is to bring about a brightening effect on the colour, while there is no doubt the operation tends to fix the colour on the cotton better. The soap effects these objects by first removing any excess of dyestuff from the cotton which has not been united with the mordant that was first fixed on the cotton, and which excess of dyestuff, if left in would dull the colour, and might subsequently give rise to stains. Secondly, there is no doubt that the soap has a tendency to enter into combination with the dyestuff on the one hand and the mordant on the other, so that a triple combination of soap, dye, and mordant is fixed on the cotton, which is faster and brighter than a simple combination of dye and mordant.

The soaping is generally effected by working or passing the dyed goods through a soap liquor of a strength of 2 lb. per 50 gallons of water at about 150° F.

The best soap for this purpose is a green-olive-oil soap, made from sulphur olive oil, and known as Marseilles soap. This is made to contain 62 to 64 per cent. of oil, with a corresponding proportion of alkali and water. A sample of such a soap examined by the author contained :—

									Per cent.
Water	.	.	.	.	.	.	.	.	27·52
Free alkali (Na_2O) .	.	.	.	.	.	.	.	.	0·59
Combined alkali (Na_2O)		.	.	.	.	.	.	.	7·44
Free fat .	.	.	.	.	.	.	.	.	1·01
Combined fat	.	.	.	.	.	.	.	.	62·06
Salts	.	.	.	.	.	.	.	.	1·38

Olive-oil soaps are fairly soluble, and leave no unpleasant odour behind them. Palm-oil soaps also work well; they are not so soluble as olive-oil soaps; they have a pleasant, characteristic odour, and do not go rancid. Tallow soaps have been and are sometimes used, but they lack solubility, and have some tendency to go rancid, hence their use is not advisable.

(3) **Calico Printers' Soap.** —Calico printers use soap to a considerable extent in the final operations of washing and clearing the printed cloths. The soap is made into a liquor of a strength of approximately 1½lb. soap to 50 gallons of water; some printers will use a stronger liquor, others a weaker liquor. Then the dyestuffs with which the cotton cloths have been printed have some influence. Thus alizarine and alizarine colours in general require a stronger soap liquor than do basic dyes, like methyl violet or methylene blue. Mordant dyes, like alizarine yellow, chrome red, etc., take a medium strength of soap liquor.

The function of the soap is not thoroughly understood. No doubt it plays several parts, which will vary according to the dye or dyes that have been printed on the cotton. In all cases it has a clearing action on the gum or starch thickening used in the composition of the printing pastes, facilitating the solution of these, and therefore their removal from the cloth. In the case of alizarine and mordant dyes in general it has a decidedly brightening and fixing action. Probably, as has already been mentioned under "Dyers' Soaps," this is brought about by a removal of excess of dyestuff that has not entered into combination with the mordant, thus helping to brighten the colour, while the fatty matter of the soap may enter into combination with the mordant, and thus tend to fix it on the cloth, at the same time bringing about a more complete combination

of mordant and dye, a triple compound of fat, mordant, and dye being formed as a kind of lake pigment which is fast and bright.

In the case of basic dyes probably the soap may remove traces of dye which has not properly entered into combination with the tannin-antimony mordant used, and so tend to make the finished print faster to washing. Possibly also some of the fatty matter of the soap may enter into combination with the antimony, etc., and help to render it more insoluble, and in that way printed fabrics may be produced which are faster to washing than would otherwise be the case.
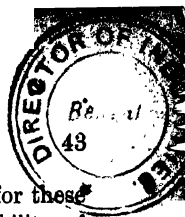
Soaps which are best adapted for treating printed calicoes and other fabrics should be easily soluble in water, and therefore oil soaps are best. They should be quite neutral (as any free alkali would be liable to change the tints of some colours and make others run), must contain no rosin, and must be such as do not leave any objectionable odour on the material,—hence cotton-seed and maize-oil soaps should not be used. The green-olive-oil soap described under "Dyers' soaps" is that most generally used. Palm-oil soap is sometimes employed, but tallow soaps are too insoluble to be really suitable for the purpose. The soaps described under "Dyers' soaps" may generally be taken as suitable for calico printing.

The question of solubility of the soaps used with calico prints is a very important one, for the more soluble the soap the more fluid is the liquor it makes, and the more easily will it penetrate into the fabric as the latter passes through the soap liquor; while, further, the temperature of the soap-bath need not be raised so high. The best and the most easily soluble soaps would be, of course, neutral potash soft soaps, and such are even used by some calico printers for their best and most expensive prints.

Calico printers' soaps should be quite free from fillings of any kind. Some of them may contain 1 to 2 per cent. of common salt or sodium sulphate, the presence of which is of no practical moment and cannot always be avoided.

While hard soaps may be used for soaping cotton, silk, and half-silk fabric, for soaping woollen and half-woollen cloths

(delaines), it is preferable to employ soft potash soaps, for these tend to more thoroughly preserve the lustre and pliability of the wool fibre. Such soaps must be quite neutral, and contain no free alkali or free fat.

IV. RELATION OF SOAP TO WATER FOR INDUSTRIAL PURPOSES.

In the various operations of wool washing, scouring, and milling; in the boiling off of silk; dyeing silk and cotton; soaping cotton prints and dyed cotton goods, etc., water is always used in conjunction with the soap, and it exercises a marked influence on the use of the latter article, first, on account of the varying degrees of solubility of the various soaps in the water; secondly and much more important, by reason of the impurities natural waters contain, as it is with natural waters that the users of the soaps have to work. Pure water,—such, for instance, as clean rain-water and water condensed from steam,—beyond exerting a solvent action on soap, has no deleterious effect.

There is no doubt that water has some chemical action upon soap, as, when soap is boiled with a large quantity of water, it dissolves to a perfectly clear solution, but on cooling, this becomes more or less turbid. Another feature which must be noticed is that there is an increase in the alkalinity of the soap when it is dissolved in cold water : this can be shown by dissolving a piece of soap in alcohol, adding a few drops of phenol-phthalein solution, and allowing the soap solution to set in a jar. On pouring water into the jar the soap gradually becomes dissolved and the solution acquires a reddish tint, showing the production of free alkali.
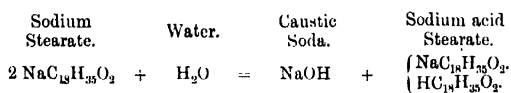
Wright and Thompson (Journ. Soc. Chem. Ind., 1885, p. 625) have conducted a series of experiments upon this subject, the action of water on soap, and have determined the amount of hydrolysis which occurs by using various quantities of water. Their results are given in the following table :—

Soap made from	Mean Molecular Weight	$x=150$	$x=250$	$x=500$	$x=1000$	$x=2000$
Pure stearic acid .	284	0·7	1·0	1·7	2·6	3·55
Nearly pure palmitic acid . . .	256	1·45	1·9	2·6	3·15	3·75
Crude lauric acid (cocoa-nut oil) .	195	3·75	4·5	5·4	6·45	7·1
Pure oleic acid .	282	1·85	2·6	3·8	5·2	6·65
Crude ricinoleic acid	294	1·55	2·2	3·0	3·8	4·3
Chiefly stearic, palmitic, and oleic acids (palm-oil tallow soap . .	271	1·1	1·55	2·6	4·1	5·3
Chiefly tallow and rosin (primrose) .	280	1·5	2·25	3·1	4·2	5·3
Cotton seed . .	250	2·25	3·0	5·0	7·5	9·5

The figures in this table are the quantities in per cent. of the alkali in the soap. It is to be noted that a tallow soap is less hydrolyzed than a palm-oil soap, and much less than a cocoa-nut oil soap, while a cotton-oil soap is more hydrolyzed than any other kind.

Lewkowitsch has made experiments on the hydrolysis of the sodium salts of oleic, palmitic, and stearic acids, 1 grm. of the anhydrous soaps being dissolved in (a) 400 cc., and (b) 900 cc. of water, and from the results he concludes that the amount of hydrolysis increases with the molecular weight of the fatty acid.

The reaction which takes place may perhaps be expressed in the following equation :—

Sodium Stearate.	Water.	Caustic Soda.	Sodium acid Stearate.

$$2\,NaC_{18}H_{35}O_2 \;+\; H_2O \;=\; NaOH \;+\; \begin{cases} NaC_{18}H_{35}O_2. \\ HC_{18}H_{35}O_2. \end{cases}$$

But the user of soap has to deal with other waters than rain water or condensed steam in order to carry out the industrial operations in which he is engaged, and such waters are not pure, the degree of impurity varying very considerably in water from different localities.

The ultimate source of all natural waters is rain, and when rain falls on the ground three things may occur. Part may pass back again into the atmosphere in the form of vapour, part

will run off the ground into the nearest brook or river, and part, probably the largest, will soak into the ground, perhaps to reappear at some other place in a well or a spring. What actually happens depends entirely on the character of the ground on which the rain falls; if it be porous, then the water will readily soak into and through it, but if it be hard and impervious, then most will run off.

Water possesses considerable solvent properties, no other substance more so; therefore when the water soaks into the ground it dissolves out some of the constituents of the rocks through which it passes, how much and of what kind depending entirely on the character of the rocks or soil through which the water passes.

Thus limestone and marly rocks contain more soluble constituents than slatey and granite rocks, hence waters from the latter are purer than from the former. Speaking generally, there are four substances commonly found in waters; the carbonates of calcium and magnesium, and the sulphates of the same two metals. Salt (chloride of sodium) is very frequent; oxide of iron is occasionally found. The following table gives the analysis of some industrial waters such as are frequently in use in steam boilers, by bleachers and dyers, etc. :—

	Parts per 100,000.				
	River Waters.		Well Waters.		Brook Water.
	(a)	(b)	(a)	(b)	
Calcium carbonate	12·49	23·41	13·13	11·86	
Magnesium carbonate	3·97	0·44	2·00	4·03	1·34
Calcium sulphate	4·66	6·14	17·39	58·01	67·63
Magnesium sulphate	—	1·83	10·07.	31·79	8·14
Sodium sulphate	2·06	—	19·56	3·79	14·26
Sodium chloride	3·89	4·36	9·91	9·07	9·67
Silica	0·61	0·60	0·89	1·20	0·89
	27·68	36·78	72·95	119·75	104·87

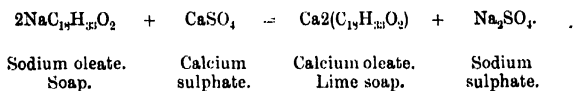The carbonates of calcium and magnesium impart to the

water the property of temporary hardness, that is, the hardness
will disappear on boiling. This is because they are kept in
solution by means of the carbonic acid gas, which all natural
waters contain, in the form of soluble acid carbonates. When
the water is boiled, the carbonic acid is driven off, and the car-
bonates are precipitated out as normal carbonates which are
not soluble in pure water, and the water is softened thereby.

The sulphates of calcium and magnesium impart the pro-
perty of permanent hardness to water, and cannot be removed
by boiling.

Unfortunately for users of water, the calcium and mag-
nesium compounds present in the water react with soap, giving
rise to the formation of insoluble lime and magnesium soaps
that form curdy masses floating in the water. These insoluble
lime and magnesium soaps are of no value for any cleansing
purposes, and the amount of ordinary soap that is required for
their formation is in effect rendered valueless from a cleansing
point of view. It follows that the less of these calcium and
magnesium carbonates and sulphates there is present in the
water, the less soap is consumed to react with them, and the
better is the water for practical use.

The reaction which takes place between the two—for ex-
ample, calcium sulphate and soap—is represented in the follow-
ing equation :—

$$2NaC_{14}H_{33}O_2 \quad + \quad CaSO_4 \quad = \quad Ca2(C_{15}H_{33}O_2) \quad + \quad Na_2SO_4.$$

Sodium oleate. Soap.	Calcium sulphate.	Calcium oleate. Lime soap.	Sodium sulphate.

This equation has a quantitative value, as it indicates the
proportions of the compounds which react with one another, and
in this case 136 parts by weight of calcium sulphate will destroy
608 parts of dry soap ; but ordinary soap contains 20 per cent.
of water, so that 136 parts of calcium sulphate will neutralize
or render inoperative 760 parts of soap ; or, to put it in another
way, 1 lb. of calcium or magnesium compounds in a quantity
of water will practically destroy 5½ lb. of soap. Now many

waters contain 35 parts per 100,000, which is equal to 24 grains per gallon of these objectionable salts; and if, say, 1000 gallons of such a water were used in a wool-washing process, there would be present 24,000 grains, and these would consume or use up 134,100 grains, or over 19 lb. of soap. These figures show the enormous soap-wasting power of calcium and magnesium compounds which may be present in water, and the importance of using water as free from them as possible; or, at any rate, when only hard water is available, taking steps to soften it by removing these objectionable bodies. This subject is too large to be dealt with here, but readers are referred to a book on "Water," issued by Messrs. Scott, Greenwood & Son.

It has been assumed above that the sulphates and carbonates of lime and magnesia have an equal soap-destroying power, but such is not actually the fact; there is a little difference, but it would complicate the position too much to discuss the case of each compound.

When hard waters are used in wool-scouring and other operations with soap, the formation of the curdy masses of calcium and magnesium soaps is liable to lead to faults in the finished article, on account of the fact that these soaps are very liable to attach themselves to the substance which is being scoured or otherwise treated, and they cannot be effectually and completely washed out; if the goods have to be subsequently dealt with, as, for instance, is the case with woollen goods which are dyed after scouring, then the latter operations are not so efficiently done as if the calcium, etc., soaps were not present. In the case of dyed goods their presence gives rise to stains of various kinds, and, if present in large amounts, they impart a greasy, objectionable feel to textile fabrics. On various counts, therefore, it is extremely desirable, in textile operations involving the use of soap, (1) to use water which is soft, or only of a few degrees of hardness; (2) if hard water only is available, to soften it before use, as the cost of so doing is less than the value of the soap which the water would destroy; or (3) treat the water with soap and soda first, and remove any scum of lime soap which may be formed before using the water.

V. TREATING WASTE SOAP LIQUORS.

In the various textile industries, particularly in the woollen and silk trades, waste soap liquors are continually being produced in the various operations of scouring and milling of wool, boiling off of silk, etc. At one time these were simply drained off into the nearest watercourse, with what effects on the purity of the water therein and the fish living in the water goes without saying. Then someone, whose name history does not record, conceived the brilliant idea of endeavouring to recover the fatty matter of these soap liquors, and, working somewhat in secret, he managed to make some money until wool-washers woke up to the fact that they might as well make money out of the waste soap liquors; while of late years the pressure of the Rivers Pollution Acts, and of the committees and boards who administer them, has caused the producers of these waste soap liquors to take steps to purify them by recovering the fatty matters, etc., which they contain.

Waste Soap Liquors from Wool-washing.—It has been mentioned already that wool is treated with soap at three different stages in the process of woollen-cloth manufacture—first, in the scouring of the raw wool, and then, after weaving, in the cleansing and milling processes. The practice of woollen manufacturers in regard to the soap liquors is various; some mix them all together, but the wisest plan is to keep the liquors from the first and the two latter operations quite distinct, as the recovered fatty matter from the liquors of the latter operations is of more value than that recovered from the liquors used in washing raw wool.

The raw wool as it exists on the sheep's back is a most impure product, and varies very much. There is first a variable amount of earthy matter, dirt—from 2 to 26 per cent. has been recorded; there is next some soapy and other matter, commonly called the suint or yolk, which is soluble in water; then there are also fatty matters soluble in ether. The following are some analyses of raw wool based on the results of Marckt and Schultz:—

				1.	2.	3.
Water	.	.	.	23·48	12·28	13·28
Wool fat	.	.	.	7·70	14·66	34·19
Suint or yolk	.	.	.	21·48	22·48	10·65
Lime soaps	.	.	.	1·74	6·21	1·39
Dirt	.	.	.	2·93	23·64	8·38
Wool fibre	.	.	.	43·20	20·64	32·11

No. 1 is from a lowland sheep, No. 2 from a Rambouillet sheep, while No. 3 is a so-called pitchy wool which contains a superabundance of fat.

The fatty matters of wool are of a most complex character. There are fatty acids of the acetic and oleic series, such as acetic acid, butyric acid, caproic acid, oleic acid, stearic acid, etc., present in the wool as potassium or lime salts; there are also present in wool the salts of lactic, benzoic, and propionic acids. There are also saponifiable neutral fats, some of which are glycerides, others are ethers resembling beeswax in composition. The wool fat consists, however, chiefly of peculiar alcoholic bodies, cholesterol and iso-cholesterol. These are not saponifiable, and are unacted upon by alkalies, and they possess the power of emulsifying with water. These bodies, when obtained in the free condition, form the basis of the product known as lanolin.

Utz ("Chem. Rev. Fett u. Harz Ind., 1906," 249 and 275) has examined a number of samples of wool fat, and finds them to have the following properties:—

	Crude.	Purified.
Specific gravity at 15° C. .	—	0·9322-0·9442
Melting point .	38·5° C.	35·5-37·1° C.
Solidifying point	—	37·5-40·0° C.
Water .	0·56 °/₀	0·32-0·51 °/₀
Ash .	0·30 °/₀	nil
Acid value .	10·65	0·28-0·7
Saponification value .	146·02 ·	84·24-98·28
Total acid value	105·58	72·88-76·38
Iodine value	23·69	15·32-17·61
Reichert Meissl .	5·91	4·68-6·88
Refractive index at 40° C. .	1·4786	1·4781-1·4822

When the raw wool is scoured or washed, all these bodies

pass into th'e liquors, along with any soap which has been used in the process. Some of these liquors are very rich in solid matter, consisting principally of grease.

The following table gives the analysis of several such liquors :—

	1.	2.	3.	4.
		Grains per gallon.		
Total solids	1380	758	1246	685
Grease	635	518	653·4	476
Alkalinity as sodium carbonate .	132·5	113·5	214·6	102

The simplest process for the recovery of the grease, and one which has long been practised, consists in collecting the liquors in large tanks, warming to about 150° F., then adding acid. Hydrochloric acid is the best for the purpose. The soaps present are decomposed, and the fatty matters rise to the top and are collected after cooling. Care must be taken that the acid be well mixed with the liquors. The greasy matters are skimmed off the top ; they are accompanied by various impurities of a solid nature, —particles of wool fibre, vegetable fibre, dirt, etc. This crude grease is first drained on filters from any water it contains, and is then placed in cloths and pressed in a hot hydraulic or screw press, when the fatty-matter flows out, leaving behind a cake of solid matter which is usable as manure. The fatty product is known as Yorkshire grease, wool grease, brown grease, etc. It varies very considerably from a pale-brown coloured, smooth, homogeneous grease with a very adhesive feel, due to the cholesterine it contains, to a dark-brown, grainy, semi-solid mass.

The following analysis of samples of good Yorkshire grease, by the writer, will give some idea of its composition .—

		1.	2.	3.	4.
Specific gravity at 15·5° C.		0·9311	0·9417	...	0·9570
Do. do. 98° C.		0·8900	0·8952	...	0·8720
Water		0·98	1·53	1·21	· 0·94
Fatty acid . . .		18·61	24·25	24·15	26·43
Saponifiable oil . .		68·62	58·25	30·02	16·86
Unsaponifiable oil . .		11·68	15·83	44·44	55·77
Mineral matter . .		0·11	0·14	0·18	trace.

The first is probably a grease obtained in the milling process, because of the large proportion of saponifiable fats it contains; the fourth is one from the wash liquors of raw wool. The melting-point of Yorkshire grease is 44° C. (111° F.).

This recovered grease from the scouring liquors of raw wool is only suitable for the preparation of lubricating greases; it has been tried for making soaps, but the results are not at all satisfactory, the soaps which are produced being poor in colour, very greasy in feel, and not working well, owing to the large proportion of unsaponifiable matter.

The waste soap liquors from the milling and fulling of woollen cloths may be dealt with in the same way. The recovered fat obtained from these liquors is purer in quality than that from raw-wool liquors; much, however, depends upon the quality of oil (see "Wool Oils," p. 110), used in oiling the cleansed raw wool before it was spun into yarn and woven into cloth. If a fairly good saponifiable oil has been employed, then the grease can be made into soap by simply boiling up with caustic soda. If, however, the oil used contained much unsaponifiable matter, the recovered grease is not suitable for soap-making. One good plan of using the recovered grease is to subject it to pressure, to separate it into liquid olein and solid stearin; the former could be used for oiling wool, the latter for making soap or candles.

When the aim is simply to recover the fatty matter from wool-scouring liquors, there is no better process than the acid treatment, provided it is carried out in the best possible way. But where it becomes a question of purifying these liquors sufficiently for the effluents to be discharged into brooks or rivers, then the acid process is not a good one, for it does not remove all impurities. The complete purification of the liquors can be effected better by the addition of such precipitants as copperas (ferrous sulphate), magnesium sulphate, calcium chloride, or alumina sulphate, which throw down almost all organic impurities; and by settling and filtration, an effluent is produced which is usually good enough to satisfy the requirements of river boards and committees. One objection to such a mode of procedure is that the fatty matters have to be recovered afterwards

by treatment with acid, which means extra time, labour, and plant, compared with the acid treatment. Still, a larger yield of fatty matter is the result. The acid liquors thus obtained are troublesome to deal with ; they may occasionally be used as precipitants for fresh lots of scouring liquors.

A good plan of working would be a combination of the two methods ; first treating the liquors with acid to obtain as much good fat as possible ; then treating the separated aqueous liquor with copperas or sulphate of alumina, settling or draining from any sediment that is formed, and running the clear effluent away, while the sludge or sediment is treated with acid to recover the fat it contains.

Boiled-off Liquor.—For centuries silk has been deprived of its "gum," the sericin of the raw silk fibre, by boiling it in soap liquor. The waste liquor so obtained is known as boiled-off liquor, and is largely used in the dyeing of silk, for it is found to have a considerable levelling or equalizing effect, and so tends to the production of level and uniform shades ; noticeably is this the case with the basic coal-tar dyes, of which magenta, safranine, methyl violet, and brilliant green are examples, and all of which may be dyed in an old boiled-off liquor. It is also used in dyeing with acid dyes, like indigo extract, scarlet, acid yellow, orange extra, cyanole, lanafuchsine, formyl violet, etc., by adding acetic or sulphuric acid to the liquor, although with these dyes the boiled-off liquor can be replaced by Glauber's salt with some advantage.

Boiled-off liquor naturally contains the gum, or sericin, of the silk, of which the raw silk contains from 20 to 30 per cent. This is a nitrogenous product, hence it is prone to decomposition ; thus, on keeping, boiled-off liquor becomes putrid and gives off an objectionable odour.

Usually from 20 to 25 per cent. of the weight of the silk of soap is used. (See "Silk Soaps," page 37.)

A sample of boiled-off liquor examined by the writer had a specific gravity of 1·002, and contained :—

> 98·5 per cent. water.
> 0·6 do. soap.
> 0·9 do. silk gum.

But of course the composition is liable to vary from time to time, as silk scourers differ from one another in the proportions of soap they use and strength of liquor they employ.

The only constituent of any value in the liquor is the fatty matter contained in the soap, but this cannot be recovered by treatment with acid, for the silk gum present seems to prevent the fatty matter from separating out, as it does from a plain soap solution on acidifying.

The best reagent to use is sulphate of alumina. A solution of 5 per cent. strength is prepared and added to the boiled-off liquor, which is cold and contained in tanks. The sulphate of alumina precipitates out both the soap and the silk gum, as a curdy mass. This is filtered off, and generally leaves the watery liquid quite clear, and in a fit condition to run away.

The mass of alumina soap and silk gum which is obtained is next mixed with a small quantity of water and hydrochloric acid, when the fatty matter separates out and collects on the surface of the aqueous liquid, and, by allowing the mass to cool down, can be easily skimmed off. The crude fat so obtained can be clarified by boiling over water, and is usually suitable to be made into soap.

The aqueous liquid from which the crude fat has been skimmed will contain the silk glue. It should be neutralized by the addition of soda and then passed through filter-beds, the effluent draining from which is ready for running off, while all impurities are retained on the filter.

Various other plans have been tried for recovering the fatty matter and otherwise dealing with the boiled-off liquor, both while fresh and after it has been used for dyeing, when, of course, it will contain some dyestuff.

A method of treating soap liquors, especially those which have been used in dyeing silk, is described by Gianoli in "L' Industria." (See "Journal, Society of Dyers and Colourists," August, 1887.) The liquors are run at a temperature of 70° to 80° C. into suitable vats, and there treated with a mixture of hydrochloric acid and ferrous sulphate (copperas). Double decomposition ensues, free fatty acid, iron soap, and a combination of albuminous matter

and iron are formed. All these collect on the top of the liquid
which is drawn off. The pasty mass of iron, soap, etc., is put
into lead-lined vats, and there boiled with about 15 per cent. of
its weight of sulphuric acid of 51° Tw. strength. The fatty acids
of the soap are set free and are perfectly pure. They may be
made into soap with caustic soda in the usual way. The acid
liquor contains sulphate of iron, and may be used for treating
fresh waste soap liquors.

Calico Printers' and Dyers' Soap Liquors.—The used soap
liquors which are obtained by the calico printer and dyer in
working many of his processes may be purified much in the
same way as the soap liquors so far discussed. Soap was for-
merly used much more extensively in this way than is the case
at the present time. A well-known Manchester firm of dry-
salters devised a process many years ago for dealing with these
waste liquors, and were in the habit of buying up the fat that
was recovered, and treating it for the purpose of making it
marketable.

A simple plan with waste soap liquors of fairly good quality,
and free from much dyestuff, is to treat them with acid at a
temperature of about 150° F. in suitable tanks. The fat collects
on the top, and can be drained off, and, if of good colour and
quality, may be used to make soap with.

If the waste soap liquors contain much dyestuff, the best
plan is to add sulphate of alumina, collect the precipitated soap,
etc., on filters, allowing the aqueous liquor to flow away. The
alumina soap is treated with dilute sulphuric acid to recover the
fat, which is used again to make soap. The acid liquors con-
tain the alumina, and may be used to precipitate a fresh quantity
of soap liquors.

When the recovered soap from any process is not good
enough to make soap with, then it may be sold to grease-makers
or to oil-distillers, who can deal with it.

VI. SOAP ANALYSIS.

Soap manufacturers and users often require to know the
actual contents of soap, etc., that any given sample of their own

or of another maker's preparation may contain. Occasionally they may desire to know more particularly the constituents of a particular sample of soap. Such information as is here alluded to necessitates for its supply a more or less full chemical analysis of the sample.

Soap, when pure, consists essentially of three substances— fat, alkali, and water—in a state of more or less intimate union. Now, as in any process of soap-making it is impossible, owing to the presence of small amounts of unsaponifiable matter, to completely saponify all the fat which is used, soap always contains the fat in two conditions—i.e. mostly combined, but a small amount free; while the alkali may be present partly free and partly combined with the fat. In the great majority of cases it suffices to determine the above constituents, together with the " titre " or solidifying point of the fatty acids, to ascertain the value of a soap.

In some cases a more elaborate analysis is required, and other constituents—rosin, silicate of soda, salt, sulphate of soda, and other bodies, which may have been added for various reasons —have to be tested for, and, if present, determined. Then, again, a soap-maker may desire to know the nature of the fats used in making the sample.

A complete analysis of a soap—particularly an industrial soap—will take cognizance of the following constituents :—

Free fat.	Sodium chloride.
Combined fat.	Sodium sulphate.
Free caustic alkali.	Sodium silicate.
Carbonated alkali.	Borax.
Combined alkali.	Mineral fillings.
Water.	Glycerine.
Rosin.	Sugar.

Notwithstanding the great advance in the practice of analytical chemistry, as applied to oils, fats, and products prepared therefrom, much still remains to be done before the analysis of soap in every.phase is brought to a state of perfection, and an analyst can boast that he has given a perfectly true report as to the exact composition of any particular sample of soap that may come under his notice.

Before commencing an analysis of any particular piece of soap, it is of great importance to obtain a good average sample of it, and herein we may briefly touch upon a point of difficulty that the soap analyst must guard against if he desires to obtain good results. If a bar of soap, especially one that has been made for some time, be cut across, it will be observed that there is on the outside a skin which is harder than the central portion of the bar.

Now if portions are taken from the outer and inner parts of the bar and analysed, it will be found that different results are obtained, the outer skin containing much less water than the inner portion, so that since it is usually the custom in soap analysis to take several portions for the different constituents, it is obvious that concordant results will not be obtained unless the analyst is exceedingly careful in selecting his sample and in cutting it up. In order to avoid this difficulty, many analysts have devised schemes for the analysis of a sample of soap from only one weighed portion. Some of these schemes have not been published, others have, and one or two of these will be noticed. One disadvantage of such schemes is that they take a considerable time to work through, and often time is of importance. Then, again, the soap is subjected to some operations which may have an effect on the character of the other constituents. Thus, for instance, supposing that, as a preliminary, the soap is dried, then the heat necessary for this purpose may bring about the saponification of some free fat with the free alkali present, and the soap would be returned as neutral when it may really be alkaline. Again, if the soap be treated for certain reasons with alcohol, the latter may also bring about the complete saponification of the last traces of free fat and free alkali.

On the whole, if care be taken in sampling and making all weighings of the portions for analysis at the same time, it will be found better, and quite as good results will be obtained, to use different samples of the soap for the various estimations.

In view of the loss of moisture at the surface of a bar or cake of soap, it is usual to cut away the surface, and take

portions for analysis from the interior, as this gives more definite figures, those obtained from the surface varying almost from day to day.

Water in Soap.—Clean thoroughly and heat for a short time in an air-bath a porcelain evaporating basin; then allow to cool in desiccator, and weigh. Cut some shavings of the soap and quickly weigh out about 2 to 3 grms. It is necessary to weigh rapidly, as the soap tends to lose its moisture during the operation. Next place the basin of soap in a hot-air oven, heated to about 105° C., for about two to three hours; take the basin out, allow to cool in desiccator, then weigh it. Next replace it in the oven for about an hour, again allow to cool, and weigh it; repeat these operations until there is no further loss of weight. The loss of weight may be taken as water, although, if transparent soap is under examination, a little of the spirit may be left in, and this will also be volatilized and reckoned with the water. To take an example—

					Grms.
Weight of basin + soap	.	.	.	.	28·368
Weight of basin	.	.	.	.	25·368
					3·000
Weight of soap and basin before drying	.	.	28·368
Weight of soap and basin after drying	.	.	27·596
Loss of weight	.	.	.	.	0·772

$$\frac{0\cdot772 \times 100}{3} = 25\cdot73.$$

In this soap, there is then 25·73 per cent. of water.

This, although the best method of determining the water in soap, is somewhat slow, taking some hours to perform.

A quicker method is that described by Watson Smith. An evaporating basin with a short length of glass rod is weighed, and into it is weighed 5 grms. of the soap to be tested. The basin and its contents are placed on a sand-bath over a bunsen burner and heated, with constant stirring, until the soap begins to give off an odour of charring, which is readily perceptible. The heating is then stopped, and the basin and its contents allowed to cool, when it is weighed, the loss being the water in the soap.

				Grms.
Weight of basin + glass rod + soap	.	.	.	36·879
Weight of basin + glass rod	.	.	.	31·979
Weight of soap taken	.	.	.	5·000
Weight of soap, etc., before heating	.	.	.	36·879
Weight of soap, etc., after heating	.	.	.	35·853
Loss of weight	.	.	.	1·026

$$1·026 \times 20 = 20·52:$$

In this sample of soap there is 20·52 per cent. of water. This method of working, carefully followed, gives good results.

Alkali in Soap.—The alkali in soap may be present in two forms, free and combined. A good sample of well-made soap should not contain any free alkali ; but it is very difficult to make a soap which shall not contain any, and so the best of soaps have frequently small traces present. It is only when special means have been taken to prevent its being present that soap is free from this constituent. The combined alkali is that which is combined with the fat to form the soap.

The free alkali may be present in the soap as hydroxide, or as carbonate or silicate. The former is the excess of the caustic alkali, used in making the soap, not removed in the finishing operations ; the carbonate, if only in small amount, may be due to carbonation of traces of caustic alkali left in the soap, or to carbonate present in the caustic lye. If the quantity is large, or if silicate is present, these will doubtless have been added to harden a "liquored" or "run" soap.

The following are the methods employed for estimating the alkali in soap in its various forms.

Total Alkali in Soap.—Ten grammes of the soap are weighed out and dissolved in 100 to 150 c.c. of water by boiling. To the solution as much methyl orange is added as will just impart a yellow tint to the liquid ; then from a burette a normal standard solution of sulphuric acid is run in until a permanent pink coloration is produced. The solution may be kept warm during the operation with advantage. Note is taken of the number of c.c. of standard acid used, and this multiplied by 0·031 and by 10 gives the percentage of total alkali, calculated as Na_2O. In-

stead of using methyl orange as indicator, a few drops of lacmoid solution may be added. This gives a blue coloration with soap solution, and the addition of standard acid is continued until this blue changes to pink.

It is customary to consider soap as a combination of soda, Na_2O, the oxide of the metal sodium, with the anhydrides of the fatty acids. In this view sodium oleate would have the formula—

$$Na_2OO \begin{cases} C_{18}H_{33}O \\ C_{18}H_{33}O \end{cases}$$
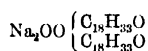
Having this view of the composition of soap in mind, it is customary on the part of chemists to calculate the free and combined alkali in soap as soda (sodium oxide, Na_2O), and accordingly the number of c.c. of standard acid used is multiplied by 0·031, which gives the amount of soda in the 10 grms. of soap, and this multiplied by 10 gives the percentage of total alkali (Na_2O) in the soap. As an example, in testing a sample of soap, the readings on the burette were as follows :—

Second reading . . . . . 32·5
First reading . . . . . 6·0
————
26·5

$$26·5 \times 0·031 \times 10 = 8·215,$$

so that the soap contains 8·21 per cent. of total alkali, as Na_2O.

An alternative method for the estimation of total alkali in soap is to incinerate 5 grms. of the sample in a platinum dish, extract the residue with boiling distilled water, and filter ; then titrate the filtrate with $\frac{N}{1}$ sulphuric acid, using methyl orange as indicator. The number of c.c. $\frac{N}{1}$ acid required $\times$ 0·031 $\times$ 20 = percentage of Na_2O.

Similar methods may be employed in the case of soft soaps, the alkali for these being calculated in terms of K_2O, of which 1 c.c. $\frac{N}{1}$ acid is equal to 0·047 grm.

Free Caustic Alkali may be determined by weighing out 2·5 grms. of the soap, and dissolving it on a water-bath in 100 c.c.

neutral alcohol. It is best to use absolute alcohol, but as this is expensive, the ordinary methylated spirit may be used if it is subjected to a purifying process, the simplest method of conducting which consists in placing some caustic soda in the spirit, allowing to stand over night, then redistilling about 90 to 95 per cent., the residue which remains in the still or retort being thrown away. Before use the alcohol or spirit should be neutralized by adding a little phenol-phthalein and sufficient caustic soda to produce a faint pink tint.

When the soap has been dissolved in the alcohol, or the latter has dissolved as much as it will, the solution should be filtered through a dry plaited filter, taking care to expose the solution to the air as little as possible. The solution should be made in a flask, and the filtering should be done through a funnel into a flask, the funnel being covered by a glass plate. When the liquid has gone through the filter, the residue must be washed several times with a small quantity of hot neutral alcohol to wash out all traces of soap, the washings being added to the main body of the filtrate.

To the alcoholic solution is now added phenol-phthalein as an indicator, when, if there be any free caustic alkali, a red colour will be obtained. The solution is now titrated with $\frac{N}{10}$ standard acid as before, until the red colour is destroyed. The percentage of free caustic alkali is calculated as Na_2O by multiplying by 0·0031 and by 40.

The alcohol only dissolves the soap and any alkali which may be present as hydroxide (caustic) alkali; any in the form of carbonate, borate, or silicate is undissolved, and remains as an insoluble residue on the filter. (*vide infra*).

Free Carbonated Alkali, Silicate, or Borate.—The residue left on the filter paper after determining the caustic alkali, is washed with hot distilled water, and the filtrate titrated with $\frac{N}{10}$ acid, using methyl orange as indicator. The number of c.c. required × 0·0031 × 40 gives percentage of free carbonated alkali, expressed as Na_2O.

Combined Alkali.—The difference between the total alkali and the sum of the two preceding determinations gives the alkali combined with fatty acids to form the actual soap. This may also be estimated directly by titrating to lacmoid or methyl orange with $\frac{N}{2}$ sulphuric acid the filtered alcoholic soap solution after neutralizing any free caustic alkali. Each c.c. of $\frac{N}{2}$ acid is equivalent to $0·0155$ grm. Na_2O, so that the number of c.c. required × $0·0155$ × 40 gives the percentage of combined alkali.

Fatty Matter.—The fatty matter of soap is present in two forms, free and combined; the former should, in the best grades of soap, be present only in trifling amount. It may comprise (1) any fat which has resisted the saponifying process; (2) any unsaponifiable matter which may have been present in the fat or oils used to make the soap; (3) any fatty material added to "superfat" the soap; and (4) any fatty matters such as mineral soap stock, which may have been added as a filling to the soap.

Soap made from bone or skin grease, or from distilled oleine, is liable to contain a good deal of unsaponifiable matter, which is very objectionable in textile soaps, not only lowering the percentage of fatty acids, but neutralizing the scouring effect of some of the combined fatty acids, and also being liable to stain the material washed. A limit for free fat of $0·6$ per cent. is a perfectly reasonable one to specify for a textile soap.

In some so-called superfatted soaps, an excess of free fat, usually present in the form of wool fat or lanolin, is purposely added, but these are not suitable for use in the textile industries.

Free Fat.—To ascertain the amount of free fat in the soap, dissolve 5 grms. in warm distilled water, and transfer to a separating funnel. Shake thoroughly with about 20 c.c. of petroleum ether, and allow to separate. If the layers separate with difficulty, an intermediate emulsion forming between them, the addition of a little alcohol will often facilitate the separation. The ethereal extract is transferred to another separator, and the

soap solution extracted with two further quantities of petroleum
ether, the ether extracts mixed, washed with a little distilled
water, and placed in a tared flask, the ether distilled off, and
after drying in the air-oven at 105° C. the residue of free fat
weighed.

Fatty Acids.—The total fat which is present in the soap
is determined by dissolving 10 grms. in distilled water, adding a
slight excess of dilute H_2SO_4, and heating on a water-bath until
the fat separates out on the top of the aqueous liquor in a clear,
transparent layer of oil.   Two plans may be followed for collect-
ing and weighing this fat.   The method commonly recommended
is, with all those soaps which will give a solid fat, to allow the
fat to cool and set into a solid cake; the aqueous liquid is now
run off and clean water added.   The mass is now heated until
the fat is once more melted, when it is again allowed to cool,
the cake of fat is separated from the wash water, dried between
sheets of filter-paper, and weighed.

When the soap is of such a character as to yield fat that will
not separate out as a solid cake, but which remains more or less
liquid or pasty, 10 grammes of white wax or of paraffin wax are
added to the fat, melted up along with it, allowed to solidify,
and, after treatment as above, finally weighed with it.   From
the final weight that of the wax is deducted, leaving the weight
of fat present in the soap.

There are some objections to this method of working, and it
requires care in execution if good and reliable results are to be
obtained.   It is difficult to remove the whole of the fat from the
sides of the glass beaker which is used in carrying out the opera-
tion, and this tends to reduce the amount of fat found.   Then
it is difficult to free the cake of fat from all traces of moisture,
and hence there is a liability from this cause to increase the
apparent weight of fat.   The two sources of error thus indicated
acting in opposite directions, may tend to neutralize one another.

A more accurate method is to wash the soap solution into a
separating funnel, add a slight excess of dilute sulphuric acid,
and extract three times with successive quantities of petroleum
ether, separating after each extraction.   The mixed ethereal ex-

tracts are then washed with water, transferred to a tared flask, and the ether distilled off, the residue, after drying in the oven at 105° C. until constant, being weighed.

By any of the processes above described there is obtained the total weight of fat in the soap. This fat will contain the free fat as well as that present in combination with the alkali in soap. The amount of the latter can be determined by deducting the amount of free fat which has previously been ascertained. The combined fat consists essentially of fatty and rosin acids, and is usually spoken of as the " Fatty Acids ".

We do not obtain them in the form in which they are present in the soap, in which they may be regarded as existing as anhydrides combined with sodium oxide (Na_2O),—but as fatty acids, i.e. anhydrides + water, and so the results are slightly in excess of the truth ; thus then an accurate analysis of soap, taking the water and fatty matter as found, the free alkali as $NaOH$ and Na_2CO_3, and the combined alkali as Na_2O, will come out slightly in excess of 100; this excess will vary according to the quantity and character of the fatty matter present, but may be taken as about 2 per cent.

To calculate the fatty acids to anhydrides the amount of fatty acids may be multiplied by 0·97, which while not quite accurate for every case, is sufficiently so for all ordinary grades of soap. The sum of the constituents should then amount to approximately 100.

If the soap contains much cocoa-nut oil, the results obtained in determining the amount of fatty matter by either of the two first methods given will be too low, owing to the oil containing fatty acids which are soluble in water, and which pass into the wash waters, and so are not collected and weighed. The method of extraction with petroleum ether, however, includes the soluble fatty acids.

Mr. J. A. Wilson recommends the following process:—10 grammes of the soap are dissolved in water and decomposed by a slight excess of dilute sulphuric acid; the glass or flask containing the soap mass is then heated until the fatty matter collects in a clear layer on the surface of the aqueous liquid. The vessel and its contents are now cooled and the cake of the fatty

acids separated out, while the aqueous layer is filtered through a wet filter-paper. The cake of fatty acids is washed three times with 250 cubic centimetres of boiling water, cooling and filtering each time. The various filtrates are collected, methyl orange is added as an indicator, and the liquor titrated with decinormal caustic soda until the pink colour changes to yellow. By this means the excess of mineral acid used in decomposing the soap is got rid of. To the liquid is added phenol-phthalein, and the titration continued until the characteristic pink colour is produced; the amount of standard soda solution used corresponds to the amount of soluble fatty acids present, and these are calculated to caprylic acid, $HC_8H_{15}O_2$ by multiplying by the factor 0·0144. The cake of fatty acids may be dried and weighed, thus giving the amount of insoluble fatty acids.

It may be mentioned here that, by collecting the fatty acids, dissolving them in neutral methylated spirit, using phenol-phthalein as an indicator, and titrating with standard caustic soda, there is obtained the amount of alkali required to combine with the fatty acids to form soap; if in previous tests more has been found, then such excess must be present in other forms.

Rosin.—This may be detected qualitatively by the Liebermann-Storch reaction. About 1 grm. of the fatty acids is dissolved by warming, in 2 or 3 c.c. of acetic anhydride, and· one drop of this solution is mixed on a white porcelain tile with one drop of 50 per cent. sulphuric acid, when, if rosin is present, a violet coloration is produced.

The proportion of rosin is best determined by the Twitchell process, in which 2 grms. to 3 grms. of the clear fatty acids are accurately weighed out, dissolved in 20 c.c. of absolute alcohol, and dry hydrochloric acid gas passed through the well-cooled solution until the gas ceases to be absorbed, which usually takes about thirty to forty-five minutes. Under the influence of the hydrochloric acid, the real fatty acids are esterified with the alcohol, forming ethyl salts, while the resin acids remain free. After standing for one hour to ensure completion of the reaction, about 100 c.c. of water are added together with a fragment of granulated zinc, and the whole boiled until the liquor becomes

clear, when it is transferred to a separator, and extracted with ether. The ethereal extract is washed with water until the wash water is free from acid, when 50 c.c. of neutral alcohol are added, and the solution titrated with $\frac{N}{1}$ soda or potash, using phenol-phthalein as indicator. Each c.c. of $\frac{N}{1}$ alkali is equivalent to 0·330 grm. of rosin. Twitchell recommended the use of the factor 0·346, but the first-mentioned figure appears to be more accurate.

Sodium Chloride in Soap.—The amount of sodium chloride present in a sample of soap may be determined in the aqueous liquor which is obtained in the titration for alkali with standard sulphuric acid after incineration. This may be done either volumetrically or gravimetrically. In the volumetric process the liquid is exactly neutralized with sodium bicarbonate, which is free from chloride, then a few drops of a solution of pure potassium chromate are added, and the liquid titrated with $\frac{N}{10}$ solution of silver nitrate until a permanent reddish colour is obtained. The number of cubic centimetres of silver solution used, multiplied by 0·00585, gives the amount of sodium chloride present in the quantity of soap taken.

If it be desired to determine the chloride gravimetrically, then the aqueous solution is heated to the boil, and sufficient of a solution of silver nitrate added to precipitate all the chloride ·as silver chloride, the precipitate is collected on a filter, well washed, dried, burnt in a porcelain crucible, and weighed. The weight of silver chloride so found, multiplied by 0·407, gives the weight of sodium chloride in the soap.

Another volumetric method for the estimation of sodium chloride, which has the advantage that it may be performed in an acid solution, is that due to Volhard. After the titration of the total alkali in the ash, with standard sulphuric acid, a few drops of concentrated nitric acid are added, followed by 25 c.c. $\frac{N}{10}$ silver nitrate, and a crystal of iron alum, the excess of silver

nitrate solution being titrated back with $\dfrac{N}{10}$ ammonium thiocyanate until a permanent blood-red colour is produced. Each c.c. of silver nitrate required is equivalent to 0·00585 grm. sodium chloride. Thus, if 2·5 grms. soap is incinerated and neutralized, and after adding 25 c.c. $\dfrac{N}{10}$ silver nitrate solution, 10·6 c.c. $\dfrac{N}{10}$ ammonium thiocyanate is required to titrate back the excess, then 25·0 − 10·6 = 14·4 c.c. is the number of c.c. silver nitrate required by the sodium chloride in the 2·5 grms. of soap, so that the percentage of sodium chloride is 14·4 × 0·00585 × 40 = 3·36.

In burning the soap, care must be taken not to heat it too strongly, or sodium chloride will be volatilized. It is only necessary to completely char the organic matter, so that a colourless aqueous extract may be obtained.

Glycerine.—This constituent may be looked for in some makes of toilet soaps, in all soaps made by the cold and pressure processes, and in soft soap.

To detect the presence of glycerine in soap, the following tests may be applied : Decompose the soap with acid and separate out the fatty matter, evaporate the aqueous liquor down to a small bulk, mix it with some borax, dip a piece of platinum wire in the mixture, and then hold it in the flame of a bunsen burner ; if glycerine be present the flame will become tinged with a deep green colour. By heating concentrated· solution of glycerine with bisulphate of potash, acrolein, distinguished by its powerful and characteristic odour, is obtained. Another test is to boil the aqueous solution down, render it faintly alkaline with caustic soda, and add to it a solution of borax which has been coloured a faint rose red by adding phenol-phthalein. The glycerine solution is added until the red colour disappears. On boiling the liquid·the colour comes back, but it again disappears on allowing the liquid to cool down. It should be stated that this test is not specially characteristic of·glycerine, as some other alcoholic bodies and some

kinds of sugar give the same reactions, but as such bodies are not usually present in soap they may be disregarded.

For the estimation of glycerine, 5 grms. of the soap is dissolved in water, decomposed with the slightest excess of dilute sulphuric acid, and the clear fatty acids filtered off and washed. The filtrate is neutralized with barium carbonate, again filtered, and concentrated if necessary, basic lead acetate solution added drop by drop as long as any precipitate is formed, again filtered, and the filtrate heated for one hour on the water-bath with 25 c.c. of a solution of potassium bichromate containing 74·86 grms. $K_2Cr_2O_7$ per litre, and 50 c.c. of 50 per cent. sulphuric acid. After cooling, the solution is made up to 250 c.c. in a graduated flask, and titrated against as much ferrous ammonium sulphate solution as has previously been found equivalent to 1 c.c. of the potassium bichromate solution. The percentage of glycerine $= \left\{ 0·25 - \dfrac{2·5}{n} \right\} \times 20$ where n is the number of c.c. of oxidized glycerine solution required to oxidize the ferrous ammonium sulphate solution.

Silicates.—These may be estimated by incinerating 5 to 10 grms. of the soap, cautiously acidifying the ash with dilute hydrochloric acid, and evaporating twice to complete dryness with a slight excess of hydrochloric acid, the residue being then heated to 150° C. for 30 minutes. After allowing to cool, extract with dilute hydrochloric acid, filter, wash, and ignite paper and contents in a tared crucible, the residue being weighed as SiO_2. From this can be calculated the amount of sodium silicate solution of any desired strength.

Sulphates may be determined in the filtrate from the silica estimation above by precipitating with barium chloride solution, boiling, filtering the hot liquid, and, after washing, igniting and weighing the barium sulphate. The weight of sodium sulphate may be obtained by multiplying the barium sulphate by 0·6094.

Sugar is present only in transparent soaps. Its presence may be detected by the Fehling test as follows: The aqueous solution of the soap, after the fat has been separated, is boiled

for half an hour with a few drops of sulphuric acid, the solution
is then neutralized with caustic soda, some Fehling test solu-.
tion is added, and the mixture boiled, when the presence of
sugar is indicated by the formation of a red precipitate of
cuprous oxide.   If it be desired to determine the amount of
sugar present, the aqueous solution is boiled with the acid, as
described above, a slight excess of caustic soda added, and the
solution heated to the boil; Fehling test solution is added as
long as a precipitate falls down, or until the liquor acquires a
blue colour, the liquid being maintained at a boil; the pre-
cipitate is next filtered off, well-washed with water, dried, burnt
in a weighed porcelain crucible, and weighed.   The weight of
copper oxide thus found, multiplied by 0·40875, gives the weight
of cane-sugar in the soap.

Starch in soap may be detected by means of the iodine test,
which produces a deep blue to blue-black colour.   The soap
solution must be neutralized before applying the test.   If the
amount is to be determined, the process is identical with that
for estimating the sugar, the copper oxide obtained being multi-
plied by 0·40816 to obtain the equivalent weight of starch.   It
is obvious that if both starch and sugar be present, both will be
found by the Fehling test, and they must be differentiated by
other tests; but it is extremely unlikely that both will be pre-
sent at the same time in a sample of soap.

When both sugar and glycerine are present in a soap, the
best method of working consists in evaporating the aqueous
solution down, then treating the residue with a mixture of
one volume of chloroform with two volumes of alcohol, which
dissolves out the glycerine; the solution is evaporated on the
water-bath, and the residual glycerine weighed.   The sugar
may be estimated in the residue left by the alcohol and chloro-
form; it is dissolved in water, and the sugar determined by the
Fehling test in the manner described above.

Dr. Albert R. Leeds' scheme for the analysis of a sample
of soap with only one weighing, first published in a weekly
technical paper, is given below, modified slightly by the present
writer.

Dr. Albert R. Leeds' Scheme of Soap Analysis.

Weigh out 5 grammes of the soap and dry at 100° C.

The loss of weight corresponds to the water.

Treat the dried soap in a Soxhlett apparatus with petroleum ether.

Ethereal extract contains the free fat, evaporate off the ether and weigh the residual fat.

Residue contains the soap and mineral matter; treat it with alcohol.

Alcohol solution contains the soap and free caustic alkali. Add a few drops of phenol-phthalein and titrate with decinormal sulphuric acid. The amount used corresponds to the free caustic alkali, which is calculated to NaOH, factor 0·004. Add water and boil off the alcohol; add a little methyl orange and titrate with normal sulphuric acid. Acid used corresponds to combined alkali, calculated as either Na_2O or Na, factors 0·031 or 0·023. Add slight excess of acid, boil, and separate out the fat.

Solution contains glycerine. Evaporate to dryness, after neutralizing with sodium carbonate, extract with alcohol, filter, place the filtrate in a weighed basin, and, after evaporating off the alcohol, weigh the residual glycerine.

Residue is the fatty matter. Dry and weigh it. Take half of it and dissolve it in alcohol, add phenol-phthalein and titrate with normal alcoholic soda. From the amount used the molecular weight of the fatty acids may be calculated. Add ether and dry powdered silver nitrate. (Gladding test, see further on). Shake well, and allow to settle.

Precipitate consists of the oleate, stearate, and palmitate of silver with excess of nitrate of silver. It may be neglected.

Solution contains resinate of silver. Filter from the precipitate, wash the latter with a little ether, transfer the filtrate to a separating funnel, add water, sufficient dilute sulphuric acid to decompose the resinate, and some petroleum ether if necessary. Separate the ether layer and run it into a weighed glass, evaporate off the ether, and weigh the residual rosin.

Residue from the alcohol contains Na_2CO_3, NaCl, Na_2SO_4, Na_2SiO_3, or corresponding potassium salts, starch, and any

mineral matters. Treat it with a little water, and filter through a weighed filter.

Solution.—Divide into four equal portions, a, b, c, and d, and test each as follows :—

    a. For Na_2CO_3, or K_2CO_3, titrate with decinormal H_2SO_4 with methyl orange, calculating the result to Na_2CO_3, or K_2CO_3.

    b. For NaCl or KCl titrate with standard $AgNO_3$, or weigh as AgCl, calculating to NaCl or KCl.

    c. For Na_2SO_4 weigh as $BaSO_4$, calculating to Na_2SO_4 or K_2SO_4.

    d. Na_2SiO_3 or K_2SiO_3. Decompose with HCl, and weigh the residual silica.

Residue contains starch and added mineral matter. Dry and filter and weigh. This gives the amount of starch and mineral matter. Determine the amount of starch by Fehling test. The mineral matter may be determined by difference.

Some difficulty is often experienced in the process of digesting the soap with alcohol if an ordinary beaker be employed. To overcome this, Spæth proposes extraction in a Soxhlett extractor with alcohol, the soap being contained in a narrow glass vessel similar to a weighing bottle, but with perforations at the bottom and in the lid. The holes at the bottom are covered with ignited asbestos fibre, over which a layer of filter paper, and finally a glass disc with fine perforations, are placed. The bottle thus prepared is dried at 105° C. for an hour, and weighed. The loss in weight gives the amount of water in the soap.

The bottle, without the lid, is then placed in the Soxhlett extractor, and its contents extracted with neutral alcohol for about six hours. After complete extraction, the bottle and its contents are dried at 150° C. and weighed, the result giving the amount of " filling material " in the soap. The determination of mineral substance, dextrin, gelatin, etc., in this is carried out in accordance with the usual methods.

Since the extraction is made with neutral alcohol, the amount of free fatty acids or alkalies in the alcohol extract can be directly titrated with standard alkali or acid.

SECTION II.

ANIMAL AND VEGETABLE OILS AND FATS.

ANIMAL SOAP OILS AND FATS.

TALLOW.

TALLOW is, or should be, derived from the fat of cows, oxen, sheep, goats, and similar animals, the best fat being taken from the thicker deposits which surround the abdomen, known generally among butchers as "the skin," although it is known by other names in some places. Anatomists call it "omentum". Tallow is also obtained from the fat surrounding the large muscles, the kidneys, and the other organs of the body. Fatty matter can be, and is, obtained from other parts of the animal, such as the intestines, bones, etc., and such fat is often sold as tallow, sometimes with a qualifying distinction as "bone tallow," at other times, and wherever possible, without such a qualifying description. Whenever tallow is dealt in as tallow, it is always understood to be the fat obtained from the parts above named, and the sale of any other kind of fat should be regarded as a fraud upon the buyer.

The deposit of tallow as it exists in the animal body is found to be contained in small cells or bladders of animal tissue. The reason for its being in this condition is that, being a liquid, and therefore able to move with every motion of the parts, it would otherwise be able to flow from the spot in which it is found. As it is taken from the body, the crude fat is known as "butcher's fat," and is usually purchased from the butcher by the tallow refiner, who, if he be located in a large town, often distinguishes between "town fat" and "country fat," the latter being usually

fresher, and therefore yielding a better quality of tallow than the former. The idea or principle which underlies all processes for the extraction of the tallow from this rough fat is to separate out by some means the animal tissue from the actual fatty matter, a process which is known as "rendering". Various methods have been adopted for rendering tallow, and will be found described in the writer's book on "Soaps," but the most important are treatment in a steel digestor or autoclave with steam (i) at a pressure of 40 lbs., and (ii) *in vacuo*.

Of fatty matters obtained from other parts of the animal body, the intestines give what is called "tripe tallow"; the feet yielding "neatsfoot oil". The processes for extracting these greases or fats do not differ essentially from those used for tallow, but, as a rule, they are obtained by simply boiling the various parts of the animal in water, and skimming the fat which is obtained, from the top of the water, where it collects; while the tripe and feet are used as food.

A great deal of fat, largely used in making soap, is now extracted from bones, and sold as "bone grease," "bone fat," "bone tallow," and, not seldom, wherever possible, as tallow. All bones do not contain tallow or fat; the best are cows' and bullocks' shank-bones, which are hollow and contain a fairly large proportion of good fat, often separately extracted and sold as "marrow tallow". The more solid bones found in the animals do not contain much fat, and scarcely pay for its extraction. Horses' bones contain so little fat that they are not worth the process of treatment.

In dealing with bones, it is therefore advisable to sort them into those which are worth treating for the fat, and those which are not worth so treating.

Tallow comes into this country from all parts of the world. Now it is a well-known fact with regard to natural products obtained from various localities that they vary somewhat in appearance, colour, odour, and consistence, etc., to say nothing of minor differences in chemical composition. Tallow is no exception to this rule, hence in the tallows which are sent into England from North and South America, Australia, India, etc.,

there are certain minor differences by which experts can tell the locality from which the tallow came.

There can scarcely be any doubt but that these differences are caused by the difference in character of the food on which the cattle feed in the different localities, and which must vary to a great extent. Commercially, tallows are distinguished according to their country of origin, and of the cattle, oxen, or sheep, or " beef " or " mutton," from which they are obtained. Russian tallow was formerly largely imported into England, but Russia has no longer sufficient for its own requirements, and now imports it. South America sends both " beef," and " mutton " tallow. It is chiefly shipped from the River Plate ports. It is of a slightly yellow colour, and usually of a fair quality, and serviceable for all uses. North American tallow is of very good quality, rather paler in colour than South American, and is much used by soap-makers. It is mostly " beef " tallow that comes from North America, but " mutton " tallow is also sent over. Australia is the principal source of the tallow which now enters this country; large quantities of both " beef " and " mutton " tallow being imported, of very good colour and quality, and this is largely used in the best classes of soap. The value of the tallow depends on its consistence—the harder the tallow and the higher its " titre," the more valuable it is. These points vary very much within certain limits, which will be presently pointed out, but Australian mutton is usually the hardest.

The chemical composition of tallow varies somewhat according to the method of feeding and the locality, as well as the kind of tallow. Tallow consists essentially of the two glycerides, olein and stearin, the latter predominating, forming from 60 per cent. in soft, to 80 per cent. in hard tallows. Palmitin is also probably present in some tallows, while there are also nearly always small quantities of animal tissue, colouring matter, and water, but these should not altogether amount to more than from $\frac{1}{2}$ to 1 per cent. of the total. Beef tallow contains more olein than mutton tallow, so that it is rather softer in consistence, and therefore better adapted for soap-making and lubricating and

for making. tallow oil, whereas mutton tallow is more suitable
for the candle-maker.

The specific gravity of beef tallow ranges from 0·935 to 0·939,
and that of mutton tallow from 0·937 to 0·940 at 60° F. (15° C.),
while at 212° F. (100° C.) the specific gravity is from 0·860 to
0·862. The melting-point of tallow varies very considerably,
usually ranging from 36° to 49° C. (97° to 120° F.) ; the lower limit
is that of a soft tallow, while the higher limit is a hard tallow;
39° C. (102° F.) is the average melting-point of tallow. After
being melted, it begins to solidify at rather lower temperatures,
from 33° to 46° C. (115° F.), but at the moment of solidifying the
temperature rises a few degrees. When pure, tallow should be
white, fairly firm, and without much odour and taste. It is
soluble in from 40 to 44 times its volume of alcohol. Generally
it contains a small quantity of free acid, ranging from 0·75 to
7 per cent., although occasionally samples with larger quantities
are met with. For soap-making, except by the "cold process,"
the presence of free fatty acid is not detrimental, but rather
otherwise, though with high acidity the price should be corre-
spondingly low, since it means a loss in glycerine; for lubricating
machinery, however, it is decidedly disadvantageous.

When melted tallow is allowed to cool very slowly at a tem-
perature of not less than 27° C. to 30° C. (80° to 86° F.), it forms
a granular mass, the stearin crystallizing out in the form of small
nodules, which can be separated from the more fluid mass by
pressure. The process is known as "seeding," and is largely
applied to the separation of the stearin of the tallow for use in
making candles, while the liquid which passes through the press
is known as "tallow oil," and is used for lubricating machinery
and for soap-making.

When boiled with caustic alkalies, tallow is converted into
soap. Of caustic soda, tallow usually takes about 13·79 to 13·85
per. cent. to completely saponify it ; while of caustic potash it
requires 19·32 to 19·38 per cent., the alkalies being in both cases
taken as chemically pure ; of the ordinary commercial products
more will be required, according to the strength of the article,
which varies very much. When the soap formed by boiling tallow

and alkali together is treated with acid, the fatty acids of the tallow are separated, and are usually found to amount to 95 per cent. of the tallow used. The melting-point and specific gravity of these fatty acids vary with the quality of the tallow. One of the most important tests for tallow is the " titre " or solidifying point of the fatty acids. The best qualities of tallow have a titre of 44° to 48° C., and the lower grades 41° to 43° C.

Tallow is frequently adulterated. Among other bodies have been used soft fats from other parts of the animal, such as bone or tripe tallows, cotton-seed oil, seal oil, stearine from wool grease, among fatty matters—to say nothing of china clay, starch, and similar products. It is by no means an easy matter to detect some of these adulterants ; cotton-seed oil stearin is very difficult to detect. The specific gravity of the fat at 100° F., and the melting-point, are some guide, while the increased proportion of solid fatty acid would be a clue to its addition. Cotton-seed oil can be detected by its reducing the specific gravity and melting-point, and increasing the proportion of liquid fatty acids, as well as by the Halphen and iodine tests. Stearine from wool grease can be detected by the tallow containing a large proportion of fatty acid, as well as by the silver nitrate test.

Bone grease can be detected by the tallow containing phosphate of lime, which is a characteristic ingredient of bone grease. The amount of mineral matter left on burning a pure tallow should be less than 0·1 per cent. The addition of such matters as china clay and starch can be detected by melting the tallow and allowing these insoluble matters to settle out. Such forms of adulteration are now rare, and show unskilful work on the part of the adulterator. Paraffin wax and scale and mineral oil are sometimes added ; these may be detected by their reducing the percentage of potash required to saponify the tallow, increasing the proportion of unsaponifiable matter, and by the sample having a low flash-point (under 400° F.).

Tallow is now rarely used for lubricating machinery. At one time it was largely used for lubricating steam-engine cylinders, but it has been superseded by the petroleum cylinder oils. It is

used now in small quantities for lubricating heavy engine bearings, bearings of rolling mills, and for making lubricating greases.

Tallow is also very largely used in the sizing of cotton yarns.

Tallow is more largely used for soap-making than any other fat that is known; it gives a good soap, hard, and of a good white colour. This, however, is modified by the colour of the tallow and the care taken in making the soap. The grain of tallow soap is good and uniform; it is not readily soluble in water, and on that account it does not lather so freely as some soaps do. On the other hand, it is not so wasteful in use, its cleansing powers are excellent, and it keeps well, not acquiring any objectionable odour or becoming rancid on keeping.

It is rather troublesome to saponify, but by the exercise of a little care on the part of the soap-maker this can be easily overcome.

Constants of Tallow.

Specific gravity at 15° C. (60° F.), 0·935 to 0·942.
     „   „   50° C. (122° F.), 0·895.
     „   „   100° C. (212° F.), 0·862.
Melting-point, 39° to 46° C. (102° to 115° F.).
Solidifying-point, 36° C. (98° F.).
Insoluble fatty acids (Hehner value), 95 to 96 per cent.
Saponification value (Koettstorfer test), 193 to 197.
Iodine value, 39 to 44 per cent.

Reichert value, 0·25 c.c. $\frac{N}{10}$ KOH.

Viscosity at 120° F.   53
    „   150° F.   35
    „   212° F.   25

Constants of Fatty Acids from Tallow.

Specific gravity at 100° C. (212° F.), 0·8698.
Melting-point, 43° to 44° C. (108° to 110° F.).
Titre, 41° to 49° C. (106° to 120° F.).
Molecular weight (combining weight), 284.
Iodine value, 40 per cent.

LARD.

Lard, as is well known, is the fat obtained from the leaf and other parts of the pig, and is almost entirely used for culinary

purposes. It is used to a limited extent in soap-making, and then only in making the best grades of soaps, where a good white colour and easy solubility are desired, lard in regard to these points ranking with cocoa-nut oil. Lard is a soft fat of a consistency equal to or slightly harder than butter, melting to a clear water-white oil; its consistency varies slightly in different samples. It is white in colour, although sometimes it may have a faint yellowish or creamy tint; its odour and taste are sweet and pleasant, and if well refined it keeps well and saponifies freely, forming a good white hard soap with soda, and a white soft soap with potash. It consists essentially of a mixture of stearin and olein in somewhat varying proportions, from 60 to 65 per cent. of olein, and 35 to 40 per cent. of stearin · there are also small quantities of palmitin present. Lard is subject to adulteration, the usual ingredients added being other fats and cotton-seed oil. Lard soap has a good white colour, uniform texture, and lathers freely in water, being superior in this respect to tallow soap; it is also free from any strong smell, and does not go rancid.

Constants of Lard.

Specific gravity at 15° C. (60° F.), 0·931.
      ,,   ,,   50° C. (122° F.), 0·881.
      ,,   ,,   100°.C. (212° F.), 0·858.
Solidifying-point, 27·1° to 29° C. (80° to 84° F.).
Melting-point, 40° to 42° C. (104° to 108° F.).
Insoluble fatty acids (Hehner value), 95-96 per cent.
Saponification value (Koettstorfer test), 195 to 199.
Iodine value, 59 per cent.
Refractive index at 60° C., 1·4542.

Constants of Fatty Acids from Lard.

Specific gravity at 100° C. (212° F.), 0·844.
Titre, 37° to 39° C. (98·6° to 102° F.).
Melting-point, 43° C. (107° F.).
Molecular weight (combining weight), 280.
Iodine value, 59 to 63 per cent.

BONE GREASE.

This fat is largely used in the manufacture of the cheap sorts of soaps, such as domestic, manufacturers', wool-scouring,

and laundry soaps, either alone or in admixture with other fats
and oils. Its preparation has already been mentioned under " Tal-
low ". As usually sold, it is in the form of a greyish-coloured
granular soft fat, its consistency being between tallow and lard.
It has a slight odour when fresh, which often develops into an
unpleasant one if the fat becomes rancid. It contains some
water, the amount varying from 2 to 6 per cent., small quantities
of animal tissue, from 0·5 to 1 per cent., the latter being rather
an excessive proportion ; the proportion of free acid in bone
grease is rather higher than in tallow, the amount ranging from
7 to 21 per cent. Then small quantities of phosphate of lime are
present, which constitutes a characteristic test for the presence
of bone grease. Two samples of such a grease examined by the
author had the composition :—

	No. 1.	No. 2.
Water . . .	3·17 per cent.	2·28 per cent.
Free acid . .	21·71 ,,	6·97 ,,
Unsaponifiable oil	0·28 ,,	0·32 ,,
Saponifiable oil .	74·84 ,,	90·28 ,,
Phosphate of lime	traces ,,	0·15 ,,
	100·00	100·00

The titre of bone fat usually ranges from 40° to 41° C.

Owing to the variable quality of bone fat, it is advisable to
test it for moisture, ash, etc., before buying.

The water it contains may, if thought necessary, be got rid
of by melting the fat, and keeping it in a melted condition for
some hours, and the phosphate of lime may be removed by
washing with dilute hydrochloric acid.

The colour of bone fat varies a great deal, but as a rule this is
of little detriment to its soap-making properties, as the colour
generally finds its way into the soap lyes, and a pale soap,
rather softer than a tallow soap, and a little more soluble in
water, is obtained. Bone-fat soap still retains some of the
odour of the fat, and so, if used for domestic soaps, some scent
is required to disguise this odour, but if used for manufacturing
soap the odour is of little consequence. Common grey mottled
soaps are largely made from bone tallow.

TALLOW OIL.

Tallow oil is obtained from tallow by melting and keeping the tallow in a warm room at about 80° to 90° F. for some hours, when the stearin it contains crystallizes out in the form of small granular particles; hence this process is known as "seeding." The seeded tallow is then placed in canvas cloths and put under hydraulic pressure, when the olein it contains flows out, together with a little of the stearin, and forms the tallow oil of commerce. It is also sold under the names of ox oil, animal oil, etc. Its chief use is for lubricating machinery, but it is used for making soap when a white soap rather softer and more soluble than a tallow soap is required. Tallow oil varies much in consistence, some samples are more fluid than others, according to the proportion of stearin which the oil contains; if there is much, then the oil is solid; if little, then it is liquid. The specific gravity varies for the same reason from 0·911 to 0·915. Tallow oil contains a varying proportion of free acid, from nothing in well-prepared samples to 15 or 16 per cent. in others. Tallow oil should be quite white when cold, or have at the most a faint yellow tint. When melted it ought to be quite clear and bright, free from any cloudiness or floating particles of any kind. It has only a slight odour of an animal fat.

LARD OIL.

Lard oil, like tallow oil, is not much used in soap-making, finding its principal use in lubricating machinery. It is prepared from lard by the same process as tallow oil is made from tallow. It resembles the last oil in its properties and uses. It is, if anything, rather lighter in colour, and has a slight odour which resembles that of lard. Its specific gravity at 15·5° C. is about 0·914, saponification value 194, and iodine value 76.

VEGETABLE SOAP OILS AND FATS.

PALM OIL.

Next to tallow, palm oil used to be the fat most used for making soaps, but it has now been displaced by cotton-seed and

other vegetable oils which are cheaper, and give a better soap for the general run of domestic purposes.

Palm oil is obtained from the fruit of various species of palm trees, natives of the oil regions of the west coasts of Africa. The tree which yields the largest proportion of the palm oil of commerce is the *Elaiis guinensis*. The fruit of the palm is about the size of a small plum, and hangs in bunches from the trees. Like the plum, it contains an outer pulpy mass and an inner kernel. From the outer pulp is obtained palm oil, while the kernel yields palm-nut or palm-kernel oil, also used in soap-making, but which has different properties from palm oil.

The natives of the oil regions employ a variety of methods for the purpose of extracting the oil from the fruit. The commonest plan consists in stacking the nuts as they are taken from the tree in heaps for from seven to ten days, when by the decomposition of some of the vegetable tissues surrounding the husk of the nuts the husk can be readily removed, leaving the internal pulp and kernel. The pulp is of a rather hard nature, and to soften it the nuts, after being husked, are thrown into pots and covered over with plantain leaves, then with earth and palm leaves. In this condition they remain for a period varying from three weeks to three months, according to the fancy or practice of the particular tribe of Africans who are making the oil.

At the end of the period named the pulp will have been converted into a soft mass. It is then thrown into pits lined with stones, where it is subjected to a pounding process whereby the pulp is separated from the kernels. The former is now thrown into boiling-pots and boiled with water, when the oil rises to the top and is skimmed off, any vegetable tissue which may accompany the pulp passing into the water; or the oil may be separated from the vegetable pulp by heating it with water, so as to melt the oil, and then squeezing the mass in bags, when the oil flows out.

The quality and consistence of the product depends partly on the particular species of palm from which it is made (but as to this point, definite information is required), but more particularly upon the care with which the process of extraction has been

carried out, and the length of time the fruit is allowed to remain in the pits.

A long steeping results in the oil being harder, but at the same time its quality is materially decreased. It acquires a rancid odour, its colour is not as bright, and it contains more free acid, indicating that a decomposition into acid and glycerine has taken place. A short steep gives a soft oil of a sweet odour and a bright colour. The process of extracting palm oil being as crude as it can well be, it is evident that the commercial article is far from being all pure fat. It may contain some traces of vegetable tissue, etc., which, being very liable to ferment, will in course of time gradually bring about the decomposition of the oil, resulting in its becoming more or less rancid, and losing its odour and colour.

Palm oil is a solid fat of about the consistence of butter. It has an orange to chocolate-brown colour which is highly characteristic, but is liable to vary very much. Salt-pond and Brass oils have usually a brownish-yellow colour ; Lagos oil is a bright orange ; Sierra Leone is rather redder. The colour is probably partly dependent upon the species of palm from which the oil is obtained in the first instance, and partly on the process of extraction. Lagos oil is the best and most neutral quality, the proportion of free acid it contains rarely exceeding 10 per cent., and the amount of water and other impurities not more than 2 per cent., and in consistency it is the softest of the palm oils. Brass, so far as freedom from impurities is concerned, comes next to Lagos oil ; it is the hardest of the palm oils, and on that account is the quality most in favour with candle-makers. It usually contains a large percentage, 53 to 65, of free fatty acid, and by far the largest proportion of palmitic acid in any variety, hence its hardness.

Salt-pond oil is one of the worst qualities of palm oil to be found on the English market, the amount of impurities often being found to amount to 20 per cent., while the free acid has been recorded by Norman Tate to be as high as 80 per cent., indicating that but little actual oil is present.

The colour and odour is usually poor. Half-jack, Bonny,

and New Calabar oils occupy intermediate positions between these oils in hardness and quality generally. Palm oil has a peculiar violet-like odour, which is communicated to the soap which is made from it.

Chemically, palm oil consists of a mixture of palmitin and olein in various proportions, with varying quantities of free palmitic and oleic acids. The specific gravity of palm oil at 15° C. varies from 0·920 to 0·926. The specific gravity at 100° C. ranges from 0·875 to 0·859, the melting-point is exceedingly variable, ranging from 25° to 36° C. (77° to 97° F.), the setting-point being a few degrees lower. When saponified, palm oil yields from 94 to 97 per cent. of fatty acids, the setting-points of which range from 41° to 46° C. (108° to 113° F.), the combining equivalent is from 273 to 274. Palm oil takes from 19·6 to 20·2 per cent. of caustic potash, KOH, or from 14 to 14·4 per cent. of caustic soda, NaOH, to saponify it.

Palm-oil soap has an orange-yellow to yellow colour, depending upon the quality of the oil from which it is made, and it also possesses the characteristic odour of the oil which has already been referred to. It is hard, not liable to go rancid, and will keep well, improving in quality in so doing; it lathers fairly well, and is a good cleanser, altogether being a first-class soap, much used by calico printers and dyers.

Palm oil may be bleached, which must be done if the oil is to be used for making a white soap. There are many processes available for this purpose, that most generally employed being Watts', by means of bichromate of potash; it may also be bleached by blowing air or ozone through it, and by other means. These processes are described in the author's book on "Soaps". Adulterated samples of palm oil are scarcely known. The author has not met with one in the course of his practice, nor is the fact that it is adulterated referred to in the text-books on oils.

Constants of Palm Oil.

Specific gravity at 15° C. (60° F.), 0·920 to 0·924.

,,   ,, •   50° C. (120° F.), 0·893.

,, •   ,,   100° C. (212° F.), 0·8586.

Melting-point 27° to 42° C. (80° to 107° F.).

Insoluble fatty acids (Hehner value), 94-97 per cent.

Saponification value (Koettstorfer test), 200.

Reichert value, 0·5 c.c. $\frac{N}{10}$ KOH.

Iodine value, 51 to 52 per cent.

Constants of Fatty Acids from Palm Oil.

Specific gravity at 100° C. (212° F.) 0·8369.

Melting-point, 50° C. (122° F.).

Titre, 41-46° C.

Saponification value, 208.

Molecular weight (combining weight), 270.

PALM-NUT OR PALM-KERNEL OIL.

The nuts or kernels of the palm fruit are collected and imported in large quantities into this country, for the purpose of pressing the oil from them. In some places a very crude method is in use for extracting the oil. The nuts are put into a pan over a fire and charred slightly; some of the oil exudes and is poured off. The roasted nuts are now ground up and boiled with water; the oil they contain rises to the top and is skimmed off. After a short boil the mass of kernel meal is reground up, mixed with a little water, and again boiled up, when more oil is obtained. This is skimmed off as before. The oil obtained by this process is of a dark colour, and is unsuitable for making good soap. Most of the oil is now expressed by means of hydraulic presses.

Palm-nut oil is of white or faintly yellowish colour, of a consistency similar to butter, resembling in odour cocoa-nut oil, from which it can hardly be distinguished. The melting-point ranges from 26° to 30° C. (78° to 86° F.).

Much depends upon the proportion of oil extracted from the kernel, the first portions which are pressed out being the softest and having the lowest melting-point, the last portions being harder and having the highest melting-point. It takes from 22 to 24 per cent. of caustic potash, or from 15½ to 17 per cent. of caustic soda, to saponify it.

In this respect it resembles cocoa-nut oil, to which also it

approximates in composition, containing a large proportion of the lower fatty acids—lauric, capric, caprylic, and caproic acids—but not to so great an extent as does cocoa-nut oil. Oudemans gives the following analysis of palm-nut oil:—

Glyceride of oleic acid . . . . 26·6
Glycerides of stearic, palmitic, and myristic acids . . 33·0
Glycerides of lauric, capric, caprylic, and caproic acids . 40·4

Palm-nut oil is fairly free from free acid, and is not very liable to go rancid.

In its specific gravity at both 60° and 212° F. it resembles closely cocoa-nut oil.

Palm-nut oil is largely used in soap-making in the place of cocoa-nut oil, and gives a soap of similar properties.

Palm-nut oil is said to be adulterated with lard, tallow, and other cheaper fats and oils; such adulteration can be detected by means of the saponification value, iodine value, or the Reichert test.

Constants of Palm-Nut Oil.

Specific gravity at 15° C. (60° F.), 0·952
   ,,   ,,   40° C. (105° F.), 0·9119.
   ,,   ,,   100° C. (212° F.), 0·8731.
Solidifying-point, 20·5° C. (79° to 80° F.).
Insoluble fatty acids (Hehner value), 91·9 per cent.
Saponification value (Koettstorfer test), 245.

Reichert value, 2·4 c.c. $\frac{N}{10}$ KOH.

Iodine value 10 to 13 per cent.
Refractive Index at 25° C., 1·4553.

Constants of Fatty Acids of Palm-Nut Oil.

Titre, 20° to 24° C. (68° to 75° F.).
Melting-point, 25° to 28° C. (77° to 80° F.).
Combining equivalent (molecular weight), 211.
Iodine value, 12-13 per cent.

COCOA-NUT OIL.

The next soap oil which claims notice is that obtained from the coco-nut, or cocoa-nut, the fruit of the coco palm, *Cocus nucifera.*

The fruit of this palm is a very useful product. It is of large size, the outer portion consisting of a fibrous mass, which is made into ropes, mats, and carpets. Inside this is the nut proper consisting of a hard outer portion useful as fuel, and, inside this again, a layer of pulpy matter of a white colour, which is that portion of the fruit patronized by the young idea at fair times. The central portion of the nut is occupied by a milky fluid. The pulp is of a very oily nature, the proportion of oil usually averaging over 50 per cent.

This pulp is dried by exposure to sun and air, and in that condition is known as "coprah," and is imported into this country in large quantities for the purpose of extracting the oil out of it. The native method of extracting the oil consists in heating the pulp with water, when the oil rises to the top and is collected. Another method, commonly followed when inferior qualities of oil only are wanted, is to heat the pulp with a little water, so as to render the oil more fluid, and then to subject the mass to pressure in a rude kind of oil-press worked by oxen. In some places the pulp is dried and then grated by means of cutting machines, and this, after being mixed or heated with water, is pressed, yielding a large quantity of a good quality of oil.

Cocoa-nut oil comes into this country from many places in South-Eastern Asia, the best being that from Cochin China. Ceylon oil ranks very close behind; Manilla oil is good; and some comes from Mauritius and the Fiji Isles.

In this country cocoa-nut oil is pressed from imported coprah, but coprah oil is not usually of as good a quality as imported oil.

Cocoa-nut oil makes its appearance in this country in the form of a white but soft fat. In Asiatic countries it is a water-white, rather limpid oil. It melts at from 20° to 25° C. (68° to 77° F.) ; its specific gravity at 60°·F. is 0·931, at 212° F. it is 0·870. Its odour is pleasant and characteristic, resembling that of the cocoa-nut. It is liable to become rancid, when its odour becomes more pronounced.

It is fairly easily saponified, and on that account it is much

employed in the manufacture of soaps by the cold process. It gives a hard white soap, possessing good lathering properties, and one which, for reasons which will be pointed out presently, works well in hard waters, or in waters which contain a good deal of saline matter in solution. It takes from 24·5 to 26 per cent. of caustic potash, or from 17·4 to 18·7 per cent. of caustic soda, to completely saponify cocoa-nut oil—a larger amount than is required for any other known fat.

Cocoa-nut oil is one of the most complex oils known, as far as regards its chemical composition: the principal fatty acid present is lauric acid $(HC_{12}H_{23}O_2)$; there is also present caproic acid $(HC_6H_{11}O_2)$, caprylic acid $(HC_8H_{15}O_2)$, capric acid $(HC_{10}H_{19}O_2)$. These acids are all soluble in water, and are volatile when distilled with steam or water.

It is the presence of these lower soluble fatty acids which causes cocoa-nut oil to require so much alkali to saponify it, and to form a soap which works with hard water; for the lime salts of these fatty acids are, comparatively speaking, soluble in water, and the alkali soaps are much more freely soluble in saline solutions than is the case with the alkali salts of oleic or stearic acids, for example. There is also present in cocoa-nut oil, myristic acid $(HC_{14}H_{27}O_2)$, palmitic acid $(HC_{16}H_{31}O_2)$, with smaller quantities of other acids of the same series, and there is but comparatively small quantities of acids of the oleic series. Of course it should be understood in speaking of fatty acids in cocoa-nut oil that these do not exist in it as free acids, but in the form of glycerides. Lauric acid has a combining weight of 200. The combining weight of the fatty acids which can be extracted from cocoa-nut oil, by saponifying and liberating the acids with sulphuric acid, ranges from 196 to 204. When these fatty acids are distilled with water, the distillate possesses an acid reaction due to the volatile or soluble acids coming over; the acidity from 100 parts of oil is·equal to 0·7 to 0·83 of caustic potash. Butter and palm-nut oil contain similar acids.

Ordinary cocoa-nut oil has very little power of absorbing iodine, taking up only 8·6 to 9 per cent., but the oil contained by the rind has an iodine value of 40, so that oils prepared from

coprah admixed with rind parings have been found to absorb up to 24 per cent. of iodine. It yields from 12 to 13 per cent. of glycerine, and from 94 to 96 per cent. of fatty acids.

In soap-making, cocoa-nut oil is largely used for making white soft soap, in conjunction with tallow; for making cold-process soaps; and for making marine and hard-water soaps. When it is known that soap is going to be used in districts where hard water prevails, it is a good policy to use a little of this oil in making the soap, for then a lather is more readily obtained, and there is not so much waste of soap by the action of the lime in the water. For toilet soaps the quantity should never exceed 25 per cent. of the stock, as a larger proportion renders the soap liable to irritate sensitive skins.

Cocoa-nut oil is comparatively easily saponified, and will take a stronger alkali than any other fat; thus, while with tallow a stronger alkali than 15° Tw. cannot safely be used for pasting, with cocoa-nut oil the lye may be 30° to 32° Tw. strong. It is this feature of cocoa-nut oil that makes it so useful for cold-process soaps. It also requires more salt to salt out, nearly twice as much as tallow or other oil soaps.

Cocoa-nut oil is seldom adulterated, and only with animal fats and greases and solid vegetable fats and stearines. Any such adulteration can be detected by alteration of the saponi-fication value, reduction of the specific gravity at 212° F., and reduction of the amount of volatile acids.

Constants of Cocoa-Nut Oil.

Specific gravity at 15° C. (60° F.), 0·930.
     „   „   40° C. (105° F.), 0·9115.
     „   „   100° C. (212° F.), 0·8736.
Solidifying-point, 16° to 20° C. (60° to 70° F.).
Melting-point, 23° to 27° C. (70° to 80° F.).
Saponification value (Koettstorfer test), 250 to 260.
Insoluble fatty acids (Hehner value), 83 to 88 per cent.
Reichert value, 3·5 c.c. $\frac{N}{10}$ KOH.
Iodine value, 8·6 to 9·3 per cent.
Refractive Index at 25° C., 1·4535 to 1·454.

Constants of Fatty Acids from Cocoa-Nut Oil.

Specific gravity at 100° C. (212° F.) 0·8354.
Titre, 21° to 25° C.
Melting-point, 24° to 25° C. (75° to 77° F.).
Combining equivalent (molecular weight), 196 to 206.
Iodine value, 9·3 per cent.

OLIVE OIL.

The olive is the fruit of the olive tree, *Olea europæa*, which grows very abundantly in those countries of Europe, Asia, and Africa that border on the Mediterranean. It is extensively cultivated in Italy, North Africa, Grecian Archipelago, Spain, Asia Minor, California and Australia. The olive is a fruit resembling the plum, and of about the same size. There are certain variations in the olive grown in various localities due to climatic differences and the mode of cultivation. The fruit is collected when just ripe, and in that condition it yields the finest quality of oil. Olive oil is yielded by the pericarp or pulp which surrounds the kernel. The kernel is also capable of yielding oil, but it is interesting to note that this is different from that given by the pulp. The olive oil is obtained from the fruit by pressure, and some portion is also separated by use of solvents. The simplest method which has been in use for a long time consists in pressing in a primitive mortar, and separating the oil which flows out. Generally, the pulp is put into a large tub or tank and subjected to pressure. The oil which flows out is known as " virgin oil ". It is of fine quality, and used chiefly for edible purposes. There is a considerable proportion of oil left in the pulp, and this is usually extracted by boiling with water, then subjecting the residual pulp to a second pressure. A rather poorer quality of oil is thereby obtained. This quality of oil is chiefly used for lubricating, soap-making, wool-oiling, dyeing, and general industries. A poorer quality is often produced by subjecting the residual cake from this second pressing to extraction by means of bisulphide of carbon. This oil, which retains the objectionable odour of the solvent, and has a dark colour, is used for the commonest purposes, and is generally known as " sulphur " olive oil.

Olive oil varies considerably in its quality. The best oils have a yellowish colour, while some of the inferior qualities are of a dark greenish-brown tint. In some cases the oil has a greenish tint. The specific gravity ranges from 0·916 to 0·919 at 60° F., the presence of much free acid lowering it. The best quality of olive oil contains usually about 2 per cent. of free acid. Certain grades of what are known as " *huiles tournants*," prepared from very ripe and fermented fruits, which are largely used in dyeing, contain as much as 25 per cent. of free acid. According to Schwarz ("Chem. Zeit.," 1913, 37, pp. 752-753) sulphur olive oils frequently contain resin, ranging in amount from 3·1 to 15·6 per cent. as determined by Twitchell's process, and probably due to oxidation of the oil in the olive marc during storage, prior to extraction. Soap made from such oil has been found to cause trouble when used in dyeing. The odour of olive oil is pleasant and peculiar, the taste is sweet and bland. When cooled down, olive oil deposits stearin, and becomes solid at 6° C. (23° F.) It requires from 19·1 to 19·6 per cent. of KOH to saponify it. It absorbs about 80 per cent. iodine, and when mixed with sulphuric acid, gives rise to an increase in temperature of 41° to 45° C. One property of olive oil is, that when mixed with sulphuric acid or nitrate of mercury, it becomes solidified, being converted into elaidin. This property is not possessed to the same degree by any other oil. Olive oil is largely adulterated, the usual adulterants being cocoa-nut, arachis, cotton-seed, and mineral oils, but the character of adulteration varies from time to time.

The presence of cocoa-nut oil reduces the iodine value, and raises the saponification value, addition of cotton-seed oil tends to increase the specific gravity, while that of mineral oils tends to reduce it; at the same time addition of the latter reduces the flashing-point of the oil.

To determine the purity of olive oil, regard must be paid to the specific gravity, Koettstorfer test, iodine value, the Maumene sulphuric acid test, and elaidin test, and the properties of the fatty acids. (See also test for arachis, pp. 90-92.)

Olive oil with caustic soda yields a soap of a smooth texture,

hard and somewhat brittle when dry, breaking with a conchoidal fracture. The colour varies with the character of the oil, good oil yielding a white to cream-coloured soap, the poorer qualities yellow to greenish soaps. These soaps are very mild, keep well, and have fairly good lathering and cleansing properties. They are much used in the calico-printing trade and for boiling-off silk, owing to their freedom from smell and comparatively easy solubility. The original Marseilles or Castile soap was made from olive oil, though some of the so-called Marseilles soap now on the market is made from cocoa-nut and arachis oils. A soft soap is often made from olive oil for use in some trades.

Constants of Olive Oil.

Specific gravity at 15° C. (59° F.), 0·916 to 0·919.
    ,,   ,,   100° C. (212° F.), 0·862.
Solidifying-point, 6° C. (23° F.).
Insoluble fatty acids (Hehner value), 93·4 per cent.
Reichert value, 0·3 c.c. $\frac{N}{10}$ KOH.
Saponification value (Koettstorfer test), 187 to 196.
Iodine value, 80 to 83 per cent.
Maumene test, 41·5° to 45° C.
Refractive Index at 15° C. 1·4704.

Constants of Fatty Acids from Olive Oil.

Specific gravity at 100° C. (212° F.), 0·8759.
Titre, 21° C. (70° F.).
Melting-point, 26° C. (79° F.).
Molecular weight (combining equivalent), 283.
Iodine value, 86 to 88 per cent.
Refractive Index at 60° C. 1·4442 to 1·4454.

ARACHIS OIL.

This oil, also known as Earth-Nut or Pea Nut oil, sometimes even as simply "Nut oil," is obtained from the nuts of *Arachis hypogœa*, a herb cultivated extensively in North America, India, and West Africa. It is largely expressed in Marseilles, and is frequently used to adulterate olive oil, to which it is very similar in properties, and in the manufacture of white Marseilles soaps. It may be.detected in olive oil by the "arachidic acid test,"

which depends on the fact that arachis oil contains about 5 per cent. of arachidic and lignoceric acids, which are absent in olive oil. Lewkowitsch's modification of Renard's test, is carried out as follows.

About 10 grms. of the oil are saponified with alkali, as described under the " titre test " (p. 165), the soap dissolved in water, excess of alkali neutralized with acetic acid, and the lead salts of the fatty acids precipitated by addition of a solution of lead acetate, filtered off, and extracted with ether, all but the palmitate and arachidate being dissolved. These latter are decomposed with hydrochloric acid, the fatty acids separated from lead chloride, and dissolved in 50 c.c. of hot 90 per cent. alcohol.

On cooling this solution, arachidic acid will crystallize out, if arachis oil is present, and the amount of arachidic acid may be estimated, if desired, by filtering it off, and washing it twice with 10 c.c. of 90 per cent. alcohol, and once with alcohol of 0·890 specific gravity. The residue on the filter is now extracted with boiling absolute alcohol, in which arachidic acid is soluble, the solution evaporated to dryness, and the arachidic acid weighed.

This amount has to be corrected by the addition of 0·0025 grm. for each 10 c.c. of 90 per cent. alcohol used in the crystallisation and washing, if the treatment has been carried out at 15° C., or 0·0045 for 10 c.c. if it was done at 20° C. Arachis oil contains about 5 per cent. of arachidic acid, so that twenty times the total amount of arachidic acid represents the quantity of arachis oil in the sample under examination. The melting point of arachidic acid is 71° to 72° C.

A more recent method of detecting and estimating arachis oil in olive oil is that proposed by Bellier and subsequently modified by Franz and Adler.

In a paper on the subject (" Analyst," 1912, p. 487) Evers recommends the following processes.

Qualitative.—1 c.c. oil is saponified in a flask attached to a reflux condenser, with 5 c.c. alcoholic potash, prepared by dissolving 80 grm. KOH in 80 c.c. water, and diluting to 1 litre with 90 per cent. alcohol. One and a half c.c. dilute acetic acid

(1 volume of glacial acetic acid with 2 volumes of water) is added together with 50 c.c. of 70 per cent. alcohol, and the liquid cooled to 15·5° C. for 5 minutes. With 5 per cent. arachis oil a distinct turbidity is produced.

Quantitative.—5 grm. oil are saponified for 5 minutes with 25 c.c. alcoholic potash, as above, 7·5 c.c. dilute acetic acid added, together with 100 c.c. of 70 per cent. alcohol containing 1 per cent. by volume of hydrochloric acid. Cool to 12-14° C. for 1 hour, filter, and wash with 70 per cent. alcohol containing 1 per cent. HCl at 17-19° C., breaking up the precipitate occasionally with a platinum wire loop. Continue washing until the filtrate no longer gives any turbidity with water, and measure washings. Dissolve the precipitate in hot 90 per cent. alcohol, using 25-70 c.c., according to bulk, and cool to a fixed temperature between 15° and 20° C. If any appreciable crystals appear, allow to stand at this temperature for 1 to 3 hours, filter, wash with a measured volume of 90 per cent. alcohol (about half the volume used for crystallisation) and finally with 50 c.c. of 70 per cent. alcohol.

Wash the crystals with warm ether into a tared flask, distil off the ether, dry at 100° C., and weigh, adding corrections for the solubility in 90 per cent. alcohol, and in 70 per cent. alcohol, the former from Archbutt's table (" Allen's Commercial Organic Analysis," Vol. II, p. 94), and the latter from figures given in the paper. If no crystals are deposited from the 90 per cent. alcohol, or if the amount is only very small, add sufficient water to reduce the alcohol to 70 per cent. (31 c.c. water to 100 c.c. of 90 per cent. alcohol). Then crystallise at 17° to 19° C. for 1 hour, filter, wash with 70 per cent. alcohol, dry, and weigh, adding correction for the solubility in 70 per cent. alcohol. In either case, if the melting point is below 71° C., the product should be recrystallised from 90 per cent. alcohol.

Constants of Arachis Oil.

Specific gravity at 15° C. (59° F.), 0·916 to 0·918.

Insoluble fatty acids (Hehner value), 93-94 per cent.

Reichert value, 0·0 to 0·5 c.c. $\frac{N}{10}$ KOH

Saponification value (Koettstorfer test), 186 to 195.
Iodine value, 85 to 100 per cent.
Refractive Index at 20° C., 1·4712.

Constants of Fatty Acids from Arachis Oil.

Titre, 28° to 29° C. (82° to 84° F.).
Molecular weight (combining equivalent), 282.
Iodine value 96 to 98 per cent.

COTTON-SEED OIL.

The oil obtained from the seeds of the cotton plant *Gossypium sp.*, originally known only as "cotton-seed oil," but now also as " cotton oil," is an important ingredient of much of the household soap now made, but is not a very suitable material for textile soaps.

Cotton is obtainable from several species of trees belonging to the genera *Gossypium* of which the most important is that grown in America, the *Gossypium barbadense ;* but the cotton tree is also grown in Egypt, India, Siam, China, the tropical portion of South America, and in other localities. The seeds of the cotton are of comparatively large size, averaging from half to three-eighths of an inch in length, by a quarter of an inch broad, and one-eighth of an inch in thickness, more or less rounded and of a greenish-grey colour. To the seeds are attached the fibres which give the cotton-tree its value, and which are imported into this country in large quantities, and woven into calico and other textile fabrics. These fibres are separated from the seed by a process known as "ginning."

To extract the oil from the seeds, in this country they are first decorticated, that is, they are passed through a mill, whose action is to break open the hull of the seed and so liberate the kernel which contains the oil of the seed. With clean seed, free from much attached cotton fibre, there.is no necessity to decorticate the seed, indeed in America it is the practice to express the oil from the undecorticated seed.

The decorticating machine consists of a hollow cylinder in which revolves another cylinder, the surface of which does not touch the surface of the outer cylinder. The inside surface of

the outer cylinder has a number of knives arranged round it, while the surface of the inner cylinder has a similar set of knives. These are so arranged that when a seed passes between the two sets of knives it is cut, the hull falling in two parts, while the kernel falls down whole, or in some mills it is cut in two. By winnowing, the heavy kernels can be separated from the light hulls, which are either used as fuel or manure.

The cotton-seed oil as it comes from the press in either system of crushing is of a dark, reddish-brown to black colour, owing to its containing a rather large proportion of colouring matter, amounting, according to Longmore, to 10 lb. to 15 lb. per ton of oil. Before the oil can be used for any purpose, this colouring matter must be removed, together with any mucilaginous and resinous matter. This is effected by treating the oil with caustic soda, which combines with any free fatty or resinous acids, and the soap formed mechanically carries down with it much of the colouring matter. The quantity of caustic soda used varies in different refineries, but amounts to from ¾ lb. to 1 lb. of 77 per cent. solid caustic soda per 100 lb. of oil. It is used in the form of solution of varying strength at different works from 10° to as much as 40° Tw.

Perhaps the best plan is to use a lye of from 12° to 15° Tw. strong. Of this about 10 lb. are required for 11 cwt. of oil. The caustic and the crude oil are mixed together in a cylindrical vessel, fitted with a closed steam coil, and having a tap at the bottom for running off the precipitated " foots ". The temperature is raised by means of steam to about 120° F., agitating thoroughly all the time either with a mechanical agitator, or by means of air pumped in by a force-pump, the air not only thoroughly agitating the oil and soda, but to some extent probably acting as a bleaching agent on the oil. After a few minutes of such treatment the oil is allowed to stand for some time, when a curdy mass of soda and colouring matter, with some soap, which has been formed by the action of the soda on the oil, will settle out. The character of the oil is then noted. If not sufficiently free from colour, more soda lye is added, 'and the treatment repeated. As a rule, not more

than one such addition is required. The whole mass is allowed to stand to settle. The clear bright oil is sold as cotton-seed oil, while the coloured mass of soda, colouring matter, and soap, termed "foots," is treated in various ways. One plan is to treat it with acid, when it is decomposed, and a dark, greasy mass comes up to the top, which can be used for making very common dark-coloured soaps; by suitable means the colouring matter can be taken out and used as a dye, though for this purpose it cannot compete with the coal-tar colours; while the fatty matter present is recovered in a form suitable for use in soap-making or candle-making. The loss in refining crude cotton-seed oil amounts to from 4 to 5 per cent.

The refined cotton-seed oil so obtained contains a large amount of stearin, and hence will, in cold weather, set almost solid. By a process of refrigerating and pressing, the stearin may be removed, and is sold as cotton stearin or oleo-margarine for various purposes, while the liquid oil is often sold under the name of "non-congealable cotton oil."

The crude cotton oil has a specific gravity of from 0·928 to 0·930. Refined cotton oil is a clear, bright oil of a pale yellow colour, but it can be obtained almost, if not quite, colourless. It has a pleasant, sweet taste, somewhat characteristic, while its odour is but slight and yet characteristic. Its specific gravity varies from 0·922 to 0·926 at 15° C., much depending upon the amount of stearin in the oil, which increases its gravity. It solidifies at from 0° to 2° C. (32° to 35° F.), the more common qualities at even higher temperatures, varying with the amount of stearin they contain. Cotton oil contains olein, stearin, palmitin, with small quantities of linolein. In its general properties it lies between the true non-drying oils, like olive oil, and the true drying oils, like linseed oil, becoming viscid on exposure to the air by absorption of oxygen. Fox, in a former number of "The Oil and Colourman's Journal," states that one gramme of cotton oil will absorb 26·4 cubic centimetres of oxygen gas more than olive oil will, but not so much as linseed oil. Consequently cotton oil cannot well be used as a lubricat-

ing oil, nor as a drying oil for paint; but as a food oil, and for soap-making, it has come into rather extensive use.

It takes 19·5 per cent. of caustic potash, KOH, or 14 per cent. of caustic soda, NaOH, to saponify it, giving a rather curdy soap. It is more difficult to saponify than tallow and some other oils, and the soap retains the lyes very much, so that it is difficult to separate the soap and lyes completely, and to obtain a perfectly neutral soap. Cotton-oil soap is much darker in colour than tallow soap, the small quantity of the colouring matter of the seed which is still left in seeming to develop a dark colour with the alkali. The soap made from this oil is comparatively easily soluble in water, and therefore lathers freely, and does not last as long as a soap made from tallow and some other fats. Another feature of cotton-oil soap is that when kept for some time it goes rancid and acquires a peculiar odour, but it takes some months for this odour to develop itself. The fatty acids, insoluble in water, have a specific gravity of 0·9494 at 100° C., a titre of 32° to 33° C., and melt at from 35° to 44° C. (93° to 111° F.).

Cotton oil is rarely, if ever, adulterated. The presence of any mineral oil can be detected by the low flash-point, which will be about, or less than, 400° F., while cotton oil does not flash below 475° F. The quantity of such adulterant can, of course, be determined by the usual tests.

Constants of Cotton Oil.

Specific gravity at 15° C. (60° F.), 0·922 to 0·925.
    ,,   ,,   at 100° C. (212° F.), 0·8725.
Solidifying-point, 0° to 1° C. (32° to 33° F.)
Insoluble fatty acids (Hehner value), 96 per cent.
Saponification value (Koettstorfer test), 191 to 196.
Iodine value 104 to 108 per cent.
Refractive Index at 20° C., 1·4720.

Constants of Fatty Acids from Cotton Oil.

Specific gravity at 100° C. (212° F.), 0·880.
Titre, 32° to 34° C. (89° to 91° F.).
Melting-point, 35° C. (95° F.).
Combining equivalent (molecular weight), 286.
Iodine value, 104 to 110 per cent.

Soya-Bean Oil.

This oil has attained considerable importance during the last five or six years, not only as a soap-making material, but also for other technical purposes, such as paint making. It is obtained from the soya bean (*Soja hispida*) which is grown very extensively in China, and utilized in a variety of ways as an article of food by the Chinese and Japanese. There are two varieties of the bean, one an olive green to brownish black colour, yielding an oil absorbing 158 per cent. iodine, the other yellow to brown in colour, yielding oil having an iodine value of 136. The oil is prepared both by expression and extraction, some soap-makers insisting on having the expressed oil, though it is liable to contain more mucilaginous or albuminous matter. It is a semi-drying oil, similar in many of its properties to cotton-seed oil, or maize oil, either of which it may replace in soap-making.

Constants of Soya-Bean Oil.

Specific Gravity at 15° C. (59° F.), 0·924 to 0·9265.
Insoluble Fatty Acids (Hehner Value) 95 to 96 per cent.
Solidifying Point, − 8° to − 16° C.
Iodine value, 131 to 160.
Saponification value, 192 to 195.
Reichert value, 0·4 to 0·75.
Refractive Index, at 20° C. 1·4745 to 1·4755.
Titre, 24° to 25° C. (75° to 77° F.)

Linseed Oil.

There is scarcely a more useful plant grown than the flax plant, known to botanists as *Linum usitatissimum*. Its fibres are converted into the textile fabric known from the earliest times under the name of " linen "—one of the oldest, if, indeed, not the oldest, of the textiles,—while its seed is usable in a variety of ways. In medicine it has wide applications. It yields an oil that has many useful properties, some of which will be considered in the present article; while, after the oil has been extracted, there remains what was at one time quite a useless bye-product. Hundreds of tons of it·were at one time

annually thrown into the river at Hull, but it is now the
valuable and well-known oil-cake of commerce, largely used for
feeding cattle. In earlier times this country was practically
dependent on Russia for its supply of seed, but at the present
day linseed is extensively grown in many parts of the world.
The greatest bulk is now grown in the Argentine; the United
States holds the second place, Russia the third, and India the
fourth. Most of that imported into this country comes from
India and the River Plate district. The seed is flattish in shape,
somewhat oval, and varies much in colour—some being pale
green, others pale brown, some reddish brown, while others
again are nearly white, and all are somewhat lustrous in
appearance. Experts can tell, on looking at a sample, whether
it has been grown on the borders of the Black Sea, the Baltic,
in Calcutta, Bombay, or on the River Plate, and from the
appearance of the samples can estimate pretty correctly what
quantity of oil each will produce. Baltic seed is often mixed
very largely with other seeds, several of which do not yield oil,
whilst others yield oil with quite different qualities from linseed.

When linseed oil of a high and pure quality is desired, the
foreign seeds have to be removed from the linseed before it is
crushed. These admixtures of foreign seeds with linseed are
sometimes natural, that is, they all grow in the same field
together, but they are as often caused by wilful adulteration.
Some low-class Baltic seed does not yield more than 20 per
cent. of oil, whilst the highest-class seed (Bombay) occasionally
yields 40 per cent. All the linseed grown in India yields more
oil than any of the seed grown in Russia. The difference in
temperature is supposed to affect the yield of oil, the warmer
climate making the seed richer in oil, whilst the colder one
makes it poorer. Linseed is manipulated in various ways, and
is afterwards subjected to pressure to expel the oil from it.
Linseed oil is a limpid oil of a greenish-yellow colour, varying
a good deal in shade, which depends partly on the care exer-
cised in the pressing of the oil, and also in its refining.

East India oil is usually paler than other varieties, while
Black Sea oil is the darkest, although poor samples of Baltic

run it very close in colour. The odour and taste of linseed oil are peculiar and characteristic, not to be mistaken for any other oil. The specific gravity of linseed oil varies somewhat, the average being 0·935, but the range is from 0·932 to 0·937, at the standard temperature of 60° F.; at 212° F. the specific gravity is about 0·881. It is soluble in about forty times its own volume of alcohol at the ordinary temperature, and in about five times its volume at the boiling-point. When exposed to cold, it does not begin to become solid until a temperature of − 27° C. is reached. It is soluble in almost all solvents, like ether, petroleum spirit, turpentine, benzol, etc.

Sulphuric acid has a powerful charring action on this oil; great heat is evolved, the temperature often rising considerably above the boiling-point of water, while a copious evolution of sulphur dioxide takes place, and a treacly mass of a dark red-brown colour is obtained. Nitric acid oxidizes it readily, though much depends upon the strength of the acid which is used.

Linseed oil has a strong affinity for iodine, the quantity absorbed depending on the source of the oil, and ranging from 175 to 205. Plate oils as a rule have the lowest iodine values, and Baltic oils the highest. In this respect linseed oil has more energetic properties than any other oil except Perilla.

Linseed oil is easily saponified by boiling with either caustic potash or caustic soda; it requires for complete saponification 18·9 per cent. of its weight of caustic potash, and 13·5 per cent. of caustic soda. With potash it yields a soft soap, clear and transparent, of a brownish-yellow colour, possessing a peculiar smell, and having good detergent properties. When the proportions of alkali and oil are carefully regulated, a neutral soap may be obtained. With caustic soda, linseed oil forms a reddish-coloured soap of a buttery consistency; on this account linseed oil is rarely if ever used in making any of the ordinary domestic hard soaps, although it does find its way into a few special soaps.

Linseed oil is the basis from which nearly all the soft soaps of commerce are made, and for this purpose no better oil can be used. A linseed-oil soft soap is of a good bright appearance,

pleasing in colour, and free from any objectionable odour, which is not the case with some other soft soaps. It retains its consistency for a considerable period, which is a point of some little advantage in soft soaps.

When a linseed-oil soap is treated with dilute sulphuric acid, the fatty acids are separated out; these acids are of a buttery consistency, melting at from 22° C. to 25° C. At the ordinary temperature they have a specific gravity of 0·923 to 0·927, while at 100° C. the gravity is 0·861 to 0·864. They are insoluble in water, but dissolve readily in alcohol, glacial acetic acid, ether, and other solvents. Their combining equivalent is very high, viz. 306, which points to the presence of acids of high molecular weight.

Linseed oil contains an acid named linolic acid, having the same formula as homolinoleic acid, which yields sativic acid when acted upon by an alkaline solution of potassium permanganate; other acids present are linolenic and isolinolenic acids, which differ from the above acid in containing two atoms less hydrogen. Perhaps the most important property of linseed oil is that of drying upon exposure to the atmosphere; this makes it very valuable in painting, but has no bearing on its use in soap-making.

Linseed oil cannot be used in oiling wool, for if so, the oil absorbs oxygen with such rapidity that great heat is developed, and there is much risk of the wool taking fire from spontaneous combustion.

Constants of Linseed Oil.

Specific gravity at 15° C. (59° F.), 0·928 to 0·941.
   ,,   ,, 50° C. (122° F.), 0·920.
   ,,   ,, 100° C. (212° F.), 0·881.
Solidifying-point, – 28° C. (– 18° F.)
Saponification value (Koettstorfer test), 192 to 195.
Iodine value, 175 to 200 per cent.
Refractive Index, at 20° C., 1·4800 to 1·4812.
   ,,   ,, at 60° C., 1·4660.

Constants of Fatty Acids from Linseed Oil.

Specific gravity at 15° C. (60° F.), 0·923.
  ,,   ,, 100° C. (212° F.), 0·861.

Titre, 19° to 21° C. (66° to 70° F.).
Melting-point, 22° to 25° C. (71° to 77° F.).
Combining equivalent (molecular weight), 307.
Iodine value, 179 per cent.

CASTOR OIL.

. The next oil which claims notice is castor oil. This is obtained from the seeds of the castor-oil plant, *Ricinus communis*, a native of India, where it grows luxuriantly. The plant is a common one in English conservatories, and so is familiar to most persons. The seeds are of comparatively large size, of a greyish-green colour, and a lustrous appearance ; they contain a large proportion of oil, nearly 50 per cent., which is extracted by pressure in the usual way, or by boiling the seeds in water. Several qualities are recognized : that extracted by pressure is the best, and sold chiefly for pharmaceutical purposes ; the average commercial qualities are imported from Calcutta, Madras, Bombay, France, and Belgium.

What is known as " first-pressure French " is about equal in quality to what is known as " seconds Calcutta ". Castor oil is a thick viscid oil ; in colour it varies from colourless in the pharmaceutical product to a greenish yellow in poorer sorts ; its specific gravity ranges from 0·960 to 0·970, the average being 0·964 ; occasionally samples are met with having a specific gravity below 0·960, but such are rare. The odour varies considerably ; the best qualities are fairly free from smell, but the poorer kinds have a nauseous odour. The taste also varies in the same way —the common qualities have a peculiar nauseous taste, from which the best kinds are free.

It does not begin to become solid until a temperature of − 18° C. (0° F.) is reached, and even then only a few flakes are deposited. The oil is distinguished from other fatty oils by its peculiar physical and chemical properties, having a very high specific gravity and a high viscosity. The relative viscosities of castor and sperm are 1248 and 56·5 respectively, which figures will convey some idea of the viscid character of this oil. It is readily soluble in alcohol, 1 part dissolving in four of rectified spirit at 15° C. (60° F.). This enables any addition of other

oils to be detected: It is insoluble in petroleum spirit or in mineral oil; though this is only correct at ordinary temperatures. On being heated, castor oil will mix with or become soluble in the petroleum spirit or mineral oil, but as the temperature cools down again the two liquids separate out. Castor oil differs from other soap-making oils in having a distinct optical activity, its optical rotation being about + 4° 50'.

Castor oil consists of a little palmitin, which separates out when the oil is cooled down, and the glyceride of a peculiar acid, ricinoleic acid, which has hitherto been found only in castor oil. This acid has the composition shown in the formula $C_{17}H_{32}OHCOOH$; it differs from the other fatty acids in containing three atoms of oxygen, and there is reason for thinking that this extra atom of oxygen is combined with an atom of hydrogen in the form of hydroxyl, as shown in the formula given above: ricinoleic acid is therefore a hydroxy-fatty acid. The presence of this hydroxyl group gives to ricinoleic acid the property of forming, with sulphuric acid, ethers, and on this property is based the use of castor oil in the preparation of olein oil for calico printers' use.

Castor oil yields about 9·1 per cent. of glycerine and 96·1 per cent. of fatty acids. These have a combining weight of 306 to 307, and a specific gravity of 0·950 to 0·951 at 60° F. They are thick, viscid, and of an oily appearance, and besides containing ricinoleic acid, they also contain palmitic acid. The oil is easily saponified with caustic soda, and yields a very soluble soap. By careful treatment a liquid soap may be obtained which is much used by dyers and cotton finishers under the name of "soluble oil". Castor-oil soap is very clear and transparent, and is therefore largely used in the preparation of transparent toilet soaps; but as it is very soluble in water, such soaps are very wasteful to use. •

Castor-oil soap has often a faint odour of the oil, and is apt to go rancid on keeping. It makes a good soft soap, but is not much used for this purpose. It takes 17·5 to 18 per cent. of caustic potash, and from 12·5 to 12·8 per cent. of caustic soda, to saponify it, rather less than the majority of fats and oils; a-

stronger lye, from 15° to 18° Tw., can be used, and it is easily boiled up, and lends itself to the cold process of soap-making with great facility.

Constants of Castor Oil.

Specific gravity at 15° C. (59° F.), 0·958 to 0·966.
   „   „ 100° C. (212° F.), 0·9096.
Solidifying point, – 17° to – 18° C. (1° to 3° F.).

Reichert value, 1·6 c.c. $\frac{N}{10}$ KOH.

Saponification value (Koettstorfer test), 176 to 180 per cent.
Iodine value, 83·6 to 86 per cent.
Acetyl value, 153·4 per cent.
Refractive index at 20° C., 1·4787.

Constants of Fatty Acids from Castor Oil.

Specific gravity at 15° C. (59° F.), 0·9509.
   „   „ 100° C. (212° F.), 0·896.
Titre, 3° C. (37·4° F).
Combining equivalent (molecular weight), 292.
Iodine value, 90 per cent.

MAIZE (CORN) OIL.

This oil has of late come into considerable prominence as a soap oil. It is obtained from the seeds of the maize plant (*Zea mays*), and is extensively produced in America, being largely made as a bye-product in the manufacture of starch and glucose from Indian corn. It is a viscid liquid of a bright amber-yellow colour, and has a faint, peculiar odour and sweetish taste, recalling that of corn flour; it has a comparatively high specific gravity, being comparable with cotton-seed oil in this respect; it is comparatively easily saponified, taking from 13 to 13·5 per cent. of caustic soda, and from 18·4 to 19 per cent. of caustic potash to saponify it; yielding a soap of yellowish colour, very homogeneous, and of good consistency, very closely resembling a cotton-oil soap of a good bright, transparent appearance, and good detergent properties; it is for making soft soaps that it will be found of most service. The oil yields on saponification and acidification fatty acids, melting at from 16° to 18° C. and solidifying at from 16° to 17° C.

Constants of Maize (Corn) Oil.

Specific gravity at 15° C. (59° F.), 0·9203.

    ,,   ,,   100° C. (212° F.), 0·8694.

Insoluble fatty acids (Hehner value), 96 per cent.

Solidifying-point,-10° C. (14° F.).

Iodine value, 116 to 123 per cent.

Saponification value (Koettstorfer test), 18·4 to 19 per cent. KOH.

Reichert value, 4·2 to 4·3 c.c. $\frac{N}{10}$ KOH.

Refractive index at 20° C.. 1·4766.

Constants of Maize Oil Fatty Acids.

Titre, 16° to 17° C.

Iodine value, 120 to 126.

RAPE OIL.

This oil is pressed from the seeds of various species of rape plants, *Brassicæ natus, Brassicæ campestris*, etc.

It is a brownish-green oil (brown rape oil), or, in the refined varieties, a yellowish oil having a greenish tint. It has a peculiar and characteristic odour. Its specific gravity varies a little, but usually ranges from 0·913 to 0·916, usually being 0·914 at 60° F. By blowing air through it, it is converted into what is known as "thickened rape oil," a very viscid oil, of specific gravity 0·970 and a peculiar odour. Rape oil takes about 17·25 per cent. of caustic potash, or 12·5 per cent. of caustic soda, to saponify it. In each case soaps are obtained which are of a greenish-yellow colour and smell strongly of the oil. It is in consequence rarely used in soap-making. Further, the soda soaps are of a pasty consistency, too soft for hard soaps. This oil is frequently adulterated, chiefly with cotton and mineral oils, both of which are comparatively easy to detect. Rape oil contains three peculiar and characteristic acids—brassic, rapic, and brucic acids,—which belong to the oleic and linolenic series of fatty acids, and they have a high molecular weight.

Rape oil cannot be used in oiling wool, for it absorbs oxygen with avidity, and is, in consequence, rather liable to bring about spontaneous combustion.

Constants of Rape Oil. .

Specific gravity at 15° C. 0·913 to 0·917.
Saponification value (Koettstorfer test), 170 to 177.
Iodine value, 99 to 102 per cent.
Insoluble fatty acids, 95 to 96 per cent.

Reichert Meissl value, 0·3 to 0·7 c.c. $\dfrac{N}{10}$ KOH.

Constants of Rape Oil Fatty Acids.

Specific gravity at 100° C., 0·8.
Titre, 11·5° to 13·5° C.
Molecular weight, 321.

WHALE OIL OR TRAIN OIL.

This oil used at one time to be largely employed in the manufacture of soft soap, especially in Scotland, the home of the fish oils, but of late its use for this purpose has decreased considerably. Whale oil, or, as it is often called, train oil, is obtained from the blubber of various species of whales. It varies very considerably, not only in composition, but in quality. There are many species of whales, and each of these may reasonably be suspected of yielding an oil which differs in some respects from the oil of other whales. Generally, however, the whalers mix the products of different whales together indiscriminately, consequently the oil from different whaling ships, capturing a variety of whales, will differ somewhat. Then, again, the methods of extracting the oil from the blubber vary very much, and this has a very considerable influence on the quality of the oil. Of late years there has been more care exercised in the extraction of the oil, and consequently the quality of the product has much improved. The old method used to be to store the blubber in tanks, and extract the oils either on land or, oftener than not, when the ship arrived home; the blubber was boiled in water, the oil rising to the top and being collected; or, blubber was allowed to drain on racks,—the former process giving the best oil, the latter the worst. This method of keeping the blubber for some time before extracting the oil resulted in its decomposition, and the products thereby formed found their way into the oil and

decreased its quality by making it of a darker colour and imparting to it a more powerful odour. As a rule, whale oil is extracted from the blubber by the process of boiling it in water, whereby a better quality of oil is obtained; one advantage of the process being that the ships can store more oil. Whale oil is a reddish-coloured oil, having a fishy odour and taste; the colour, odour, and taste vary in different oils. Its specific gravity is about 0·925. When cooled down, many samples of whale oil deposit some stearin as a brownish-coloured mass, smelling of fish. It takes about 18 to 19 per cent. of caustic potash, and about 13·5 to 14 per cent. of caustic soda, to saponify it. The potash soaps are of a brownish-red colour and have a fishy odour, and are very soluble in water. The soda soaps have a dark-red colour and fishy odour, and are rather soft in consistency; for the latter reason whale oil cannot well be used in the preparation of hard soaps. Whale oil contains notable quantities of valeric acid, which is one of the volatile members of the stearic series of fatty acids.

SECTION III.

GLYCERINE.

GLYCERINE is a water-white, very viscid liquid, having a specific gravity when pure of 1·2665 at 15° C.; but it has such an affinity for water that it is difficult to obtain absolutely anhydrous glycerine, and the ordinary commercial substance generally has a specific gravity of 1·260 to 1·263, and contains a little water. It has a sweet taste, and was originally known in consequence as the "sweet spirit of oils," and in the glycerine industry the crude material is known as the "sweet water." With water it mixes in all proportions. The following table, showing the specific gravities and strengths of various mixtures of these two liquids, will be found useful :—

TABLE OF SPECIFIC GRAVITIES AND STRENGTHS OF AQUEOUS SOLUTIONS OF GLYCERINE.

Specific Gravity. 15° C.	Per cent. of Glycerine.	Specific Gravity. 15° C.	Per cent. of Glycerine.
1·2650	100	1·1990	75
1·2625	99	1 1855	70
1·2600	98	1·1715	65
1·2575	97	1·1570	60
1·2550	96	1·1430	55
1·2525	95	1·1290	50
1·2499	94	1·1155	45
1·2473	93	1·1020	40
1·2447	92	1·0885	35
1·2421	91	1·0750	30
1·2395	90	1·0620	25
1·2341	88	1·0490	20
1·2287	86	1·0365	15
1·2233	84	1·0240	10
1·2179	82	1·0120	5
1·2125	80		

Glycerine is soluble in alcohol, but only slightly so in æther. A mixture of equal volumes of chloroform and alcohol dissolves it, but it is insoluble in chloroform, benzine, petroleum spirit, and oils. It is a powerful solvent for salts, etc., being nearly equal to water in this respect.

Anhydrous glycerine is a crystalline solid, melting at 17° to 20° C., igniting at 150° C., and boiling at 290° C. It is composed of carbon, hydrogen, and oxygen in the proportions indicated by the formula $C_3H_8O_3$; in its relationships it belongs to the alcohol group of organic compounds, has basic properties, and with the monobasic acids, such as hydrochloric acid, oleic acid, acetic acid, it is capable of forming compounds containing one, two, or three equivalents of the acids, the compound containing three equivalents being the normal one; hence glycerine must be a tribasic alcohol containing three equivalents of the radicle hydroxyl OH, and therefore having the formula—

$$C_3H_5 \begin{cases} OH \\ OH \\ OH \end{cases}$$
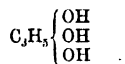
and is essentially the hydroxide of the radicle glyceryl.

It may be mentioned that although by a looseness of expression, which is very common, glycerine is often spoken of as "the base of oils and fats," yet glycerine as such does not exist in the oils, but is formed during the various processes of saponification by the combination of the real base glyceryl C_3H_5 with the radicle hydroxyl. The oils and fats are salts of this basic radicle glyceryl. Heated with strong sulphuric acid or with acid potassium sulphate it is dehydrated, and acrolein (acrylic aldehyde) C_3H_5COH, is evolved, recognizable by its peculiar odour.

Nitric acid acts on it energetically, forming a variety of products; nitro-glycerine, oxalic acid, glyceric acid, etc., being formed according to the strength of the acid used and the manner in which the operation is carried out. Heated with potassium permanganate in the presence of caustic potash, glycerine is converted into oxalic acid and carbonic acid, and, as this reaction takes place in a definite manner, it has been

proposed to take advantage of it for the quantitative estimation of glycerine.

When glycerine is heated with organic acids combination takes place, and ethers are formed known as "glycerides," and these have the special termination "in," as *acetin, olein, stearin* and *palmitin*, with the prefix "mono," "di," and "tri," to show how many equivalents of the acid are combined with one equivalent of the base. The formation of the glyceride, acetin, when glycerine is heated with acetic anhydride, is the basis of the method now usually employed for the estimation of glycerine in concentrated solution. For dilute solutions, the bichromate method described under "Soap Analysis," p. 67, is the best to use. Chemists, to show the analogy between glycerine and the alcohols, have given to it the systematic name "glycerol," but it has been thought better to use the more familiar name "glycerine" here.

SECTION IV.

TEXTILE OILS.

OILS are employed in every branch of the textile industries—in the treatment, spinning, and weaving of cotton, linen, jute, hemp, wool, and silk fabrics, and in the dyeing and printing of the same fabrics for a variety of objects; and it is intended here to discuss the uses of the oils in these trades. There is, however, one use to which oils are put that will not be here touched upon, and that is in the lubrication of the machines used in the spinning, weaving, etc. of the textile fabrics. This subject has already been dealt with in the author's "Lubricating Oils, Fats, and Greases," and to that book the reader is referred.

WOOL OILS.

The first treatment which the wool fibre undergoes in its transformation from the raw or loose wool, as it comes from the sheep's back, to the finished textile fabric, is that of scouring or cleansing, which is done by using soda or potash, with or without soap, with the object of removing the grease and dirt with which the wool is impregnated, the impurity ranging from 25 per cent. in the best and cleanest grades of wool to 60 per cent. in the commonest grades of greasy or pitchy wools.
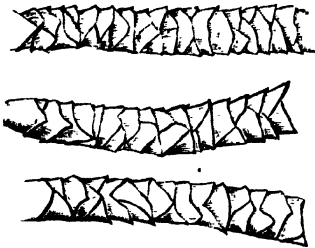
Wool thus cleansed cannot, however, be conveniently spun or woven. The wool fibre has

FIG. 5.—The Wool Fibre.

a scaly structure, shown in Fig. 5, taken from Franklin Beech's
(110).

" Dyeing of Woollen Fabrics," [1] and the scales on one fibre are liable to interlock with those of another fibre during the many manipulations through which the wool passes while being spun and woven ; and this interlocking prevents that free motion of the fibres which is necessary for a perfect woollen thread to be spun.

In order to prevent this interlocking taking place the wool is oiled before it is spun, this oiling process being commonly called " batching." The oldest method of carrying out this operation was to spread the wool in layers on the floor of a room and to sprinkle it with the oil, then to put another layer of wool down and to sprinkle this, and so on until all the wool has been treated, when it is more or less raked about or piled into heaps with the object of getting the oil uniformly distributed through the mass of the wool. A more modern plan is to attach an oiling arrangement to the first machine the wool has to go through in order to spin it into a thread.

The oil at first applied to this purpose, and still largely used, was olive oil (see page 88), but this is expensive, and other cheaper oils were often substituted —rape oil, nut oil, etc. Then there was introduced oleic acid, in more or less crude qualities, a bye-product in the manufacture of glycerine and stearic acid from tallow ; then the recovery of the soap and grease from the waste wool washings, and the treatment of the recovered grease— " brown " or " Yorkshire " grease, as it is called—by distillation, caused the introduction of so-called wool oils or oleines, oily bodies of somewhat complex composition. Then under the name of " wool oils " there are used compounded oils formed by blending or mixing various oils together with a view of producing a cheaper article. Some of these oils—olive oil, cotton oil, rape oil, and linseed oil—will be found described under the head of " Animal and Vegetable Oils."

Many kinds of oil and oily products are available, and are in use for oiling wool, either alone or mixed together. In the choice of an oil for this purpose several considerations have to be taken into account. Simply regarded from the point of

[1] Scott, Greenwood & Son, London.

view of lubricating the wool fibre to enable it to be properly spun into yarn and woven into cloth, almost any kind of oil may be used, from the cheapest of hydrocarbon oils to the most expensive of vegetable oils. A discussion of these considerations will be of interest before dealing with the various kinds of wool oils in detail.

One of the first considerations of the wool manufacturer is the element of cost. The cheapest oils are the so-called mineral or hydrocarbon oils obtained from Scotch shale, American and Russian petroleums, and rosin by a variety of processes, *vide* the Author's "Lubricating Oils, Fats, and Greases," the better refined and heavier grades of which are suitable for oiling wool when simply regarded as lubricants; but other considerations come into play which militate against their use by themselves for this purpose, as will be seen presently. The lighter grades are not suitable, not possessing sufficient lubricating power.

The next class of oils as regards cost are the so-called oleines obtained by the distillation of recovered greases, or Yorkshire grease, and will be found described later on. These are much used, and are, on the whole, very serviceable, although not perfect oils for the purpose.

Then comes the oleic acid, supplied in various grades of purity, and often under the name of "cloth oil," which is obtained as a bye-product in the manufacture of glycerine and stearine from fats. These oleic acids are very satisfactory, and can safely be used for oiling wool.

Lastly, there are the various animal and vegetable oils such as lard oil, tallow oil, olive oil, cotton oil, nut oil, etc., which are expensive; some are very suitable, in particular olive oil, which forms the typical wool oil.

A very important consideration in the selection and use of an oil for wool is connected with the operations of wool manufacture following on those of spinning and weaving. Woollen yarns and woollen cloths have to be dyed, and before this can be done the oil with which the wool has been treated must be removed. All oils can be extracted from wool by the use of ethereal solvents like benzoline, benzol, ether, carbon bisulphide,

carbon tetra-chloride, etc., and such solvents have been used with more or less success. Unfortunately the solvents benzoline and benzol, which are cheap, are very inflammable, and a perfectly satisfactory extraction apparatus adapted to their use and free from risks of explosion has not as yet been devised; while carbon tetra-chloride, which is free from this serious defect, is rather expensive. One trouble with all of them is that, owing to their very volatile character, it is difficult to construct an apparatus which will not permit much leakage, and therefore loss of solvent taking place.

The process most commonly adopted for extracting the oil from the wool is a scouring one, employing soap as the principal agent, with or without the use of soda or potash. In this process advantage is taken of two factors—first, the emulsifying power of soap solutions on oils; second, the saponifying action of soda or potash on the oils. The more perfectly the emulsifying and saponifying actions go on, the more perfectly will the oils be removed from the wool. It is essential for perfect dyeing that all—or, at any rate, nearly all—the oil be removed or otherwise the dye will be but imperfectly taken up by the wool, and streaks and patches on the material will be produced. The paraffin, petroleum, or rosin oils are not saponifiable: hence it is found that scouring wool, oiled with these oils, with soap and soda does not entirely remove them from the fibre; and for this reason they cannot well be used for oiling wool, although they are cheap.

The oleines previously referred to also frequently contain products which are unsaponifiable: if the quality is not excessive, it has no strong influence in retarding the scouring action of the soap liquors; but if the quantity becomes excessive, then there is a great liability for some of the oil to be left in the wool, and in that case perfect results in the dyeing and finishing of the fabric cannot be obtained.

Sometimes cheap grades of " wool oils " are made by blending fatty oils, oleines, and hydrocarbon oils together; if the proportion of this last be too great, then these blended oils are not suitable for the purpose.

8

The fatty oils and oleic acid, being perfectly saponifiable, make the most satisfactory substances for oiling wool.

Another consideration is the question of the inflammability of the oils and the production of spontaneous combustion of the oiled wool. Several cases of fires have occurred in wool mills which could only be accounted for by oily wool spontaneously breaking out into flame. Experiments made on wool and cotton with different oils have shown that oils vary very much in this respect.

The fatty oils are divisible into three groups, without, however, any very marked line of division. There are, first, drying oils,—those which, like linseed oil or poppy-seed oil, when exposed in thin films to the air become dry and hard. Second, those which, like olive, sperm, or lard oil, always remain soft; these are the non-drying oils. And, thirdly, there are oils which become viscid and thick, but not dry—the semi-drying oils, as they are called.

This property of drying appears to be closely connected with the power of the oils to absorb oxygen; thus Fox has shown ("Oil and Colourman's Journal," 1884, p. 234) that linseed oil will take up 191 c.c. of oxygen for each gramme of oil, while olive oil will only take up 8·2 c.c., and cotton-seed oil 24·6 c.c.

The absorption of oxygen by oils leads to the development of heat. This is greatest when the absorption is greatest. When a little linseed oil is poured over a lump of cotton, the amount of surface exposed is very great, and consequently the action of the oxygen is great also. The heat that is developed may rise so high that the cotton will become charred, and not unfrequently burst into flames. This spontaneous combustion of oily fibre is a feature of great interest in the use of oils in textile mills. In these there are always large masses of cotton, wool, etc., lying about in heaps or covering the machine as fluff. Should these become covered, accidentally or otherwise, with oil, and other conditions be favourable, then the oxidation of the oil may go on so rapidly and to such an extent that the fibre will burst into flame, and a fire is the result.

Now it has been found that only the fatty oils have this pro-

perty, of causing spontaneous combustion; the hydrocarbon oils, having no property of absorbing oxygen and combining with it, cannot cause spontaneous combustion; and, further, it has been shown by Galletly that mixing hydrocarbon with fatty oils prevents the latter giving rise to the spontaneous combustion of fibrous bodies.

Thus Galletly obtained the following results by saturating a handful of cotton waste with various oils, wringing well to get rid of superfluous oil, then placing the oily waste in a chamber kept at a temperature of about 150° F., at which oxidation begins :—

Boiled linseed oil.—One sample fired in 75 minutes, another in 105 minutes.

Raw linseed oil.—Two samples fired in four and five hours respectively.

Rape oil.—Sample put up at night was found to have been wholly consumed, box and waste, by next morning.

Olive oil.—Two samples fired in five and six hours respectively.

Lard oil fired in 100 minutes.

Sperm oil refused to ignite or to char the waste.

Mineral oils absolutely refused to ignite, and mixtures of 80 rape and 20 mineral, and of 50 seal and 50 mineral did not, when placed in a warm chamber, develop a temperature sufficient to char the cotton.

W. M'D. Mackay has described ("Journ. Soc. Chem. Ind.," 1896, page 90) a form of apparatus for determining the degree of power possessed by various oils and oily products to cause spontaneous combustion.

It consists of a cylindrical water-bath, made of copper, and tinned inside.

A section of the apparatus is shown in Fig. 6.

Its dimensions are—Outside, 8 in. high, 6 in. diameter; inside, 7 in. high, 4 in. diameter. Pipes A and B, $\frac{1}{2}$-in. internal diameter and 6 in. long, measured from the lid. The depth inside with the lid on is $6\frac{1}{4}$ in. A lid (Fig. 7), packed with asbestos wool, fits on the top, and the tubes A and B serve to ensure a current of air down B and up A. Care should be taken in using the apparatus that the steam from the water jacket is neither sucked down B nor warms A. C is a cylinder made of a piece of wire gauze 24 to the inch, forming a roll 6 in. long and $1\frac{1}{2}$ in. diameter. In the cylinder is placed seven

grammes of cotton wool (ordinary bleached cotton wadding)
previously soaked with fourteen grammes of the oil under
examination, the wool occupying the upper 4½ inches of the
cylinder.
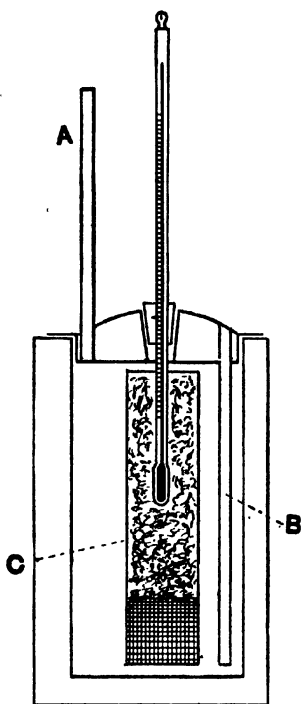
FIG. 6.   FIG. 7.
Mackay's Spontaneous Combustion Apparatus.
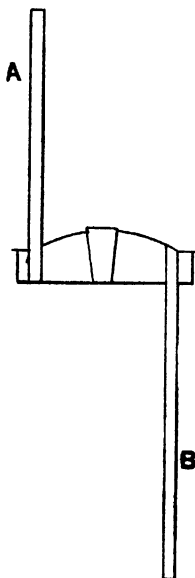
The water is brought to the boiling-point, and a thermometer
inserted in the oily wool contained in the gauze cylinder, which
is then placed in the bath, the thermometer being allowed to
protrude through a cork in the opening shown in the lid.   The
bath is left boiling, and the temperature attained read after one
hour.

Any oil tested in this apparatus attaining a temperature of
100° C. before the expiry of one hour may be regarded as dan-

gerous. In the table are given details as to the results of experiments made with cotton and olive oils, fatty acids from same, various commercial oleines, etc. It is of interest to note that fatty acids are more liable to cause spontaneous combustion than are neutral oils, while the addition of mineral oil decreases the tendency to spontaneous combustion.

Column E is not of much importance. In some cases the cotton fired, the thermometer being taken out when the temperature was observed to rise rapidly; in other cases, when probably firing would have taken place could the air have penetrated with sufficient rapidity to support active combustion, the temperature, after a rapid rise, began to go down, the experiment then being stopped. In column E, I have given the last recorded or the maximum temperature attained in each case.

The columns of importance are C and D. Any oil that disappears from column D, i.e. has either fired or attained a maximum temperature of over 200° C. before the expiration of two hours, may be regarded as dangerous: indeed, the first fifteen experiments may be taken to show that the oils in question are dangerous.

Nos. 16, 17, 18, and 19 are doubtful. The Belgian oleine, No. 19, for instance, though not rising above 100° C. in four hours, fired in five hours twenty minutes.

Nos. 20, 21, 22, 23, 24, and 25 may be taken as types of safe oils, the temperature in these cases not rising much above that of the bath, and after four to five hours declining.

The last, No. 25, is curious, as showing how a very dangerous oil, as shown in Nos. 2 and 3, becomes safe when 25 per cent. of a heavy hydrocarbon oil is mixed with it.

With regard to concordance of the results obtained, it may be mentioned that there are given here the results of all the experiments made with this apparatus. Thus Nos. 2, 3, 4, 5, 6 to 8, 9, 10, 11, 12 to 13, 14 to 21, 22, 23, 24 form groups by which the reliability of the methods may be estimated. Nos. 2, 3, and 4 show the greatest discordance.

At the instigation of the New England Cotton Manufacturers

No.	A. Oil Examined.	B. Temp. in 1 hour. °C.	C. Temp. in 1 h. 30 m. °C.	D. Temp. in 2 hours. °C.	E. Maximum Temperature. °C.	E. h. m.	F.
1.	Cotton-seed oil fatty acids, pure	151	215	...	215	1.25	...
2.	Olive oil fatty acids, pure	104	210	...	335	1.50	...
3.	„ „ another sample	113	194	...	208	1.40	
4.	„ „ same as 3	98	108	203	272	2.30	...
5.	„ „ 95 per cent. oleine	102	192	...	213	1.44	Free fatty acids, 56·5 per cent. — Unsaponifiable 4·9 per cent.
6.	„ „ same as 5	102	203	...	218	1.35	„ — „
7.	„ „ 98 per cent. oleine	110	180	...	180	1.30	„ 98·1
8.	Cotton-seed, pure	100	164 h. m. 1.25	...	234	1.35	„ 0·5
9.	„ „ the same sample	111	272 1.25	...	272	1.25	„ „
10.	„ „ „	109	224 1.15	...	224	1.15	„ „
11.	„ „ „	111	225 1.35	...	279	1.40	„ „
12.	Cotton-seed oil, pure	105	228 1.25	...	228	1.25	„ 0·0 — Neutralized with soda and washed.
13.	White Australian oleine	97	104	116	280	2.25	
14.	„ same as 13	96	103	118	308	3.10	
15.	Oleine	95	102	194	228	2.7	„ 7·4 — Unsaponifiable 10·7 per cent.
16.	„ 93 per cent. oleine, French	95.5	100 1.35	104.5	142	3.15	„ 63·5
17.	„ 97 „ „	95	98.5	100.5	181.5	4.14	„ 75·1 — 22·9
18.	Australian oleine	94.5	96	105	190	3.0	„ 90·3 — 2·2
19.	Belgian oleine	92	94	94	297	5.20	„ 90·0 — 6·4
20.	Oleine	94.5	96	97.5	105.5	5.15	„ 4·7 — 35·8
21.	Olive oil	96	97.5	97.5	102	4.15	„ 0·0 — Neutralized with soda and washed.
22.	„ same as 21. From same sample	95.5	97	97.5	108	4.0	„
23.	„ „	95	97	97	104	5.0	„ 1·0
24.	„ same as 23	Not noted.	Not noted.	96	103	5.30	„ roughly.
25.	75 per cent. olive fatty acids, same as 3 and 4, mixed with 25 per cent. American mineral.	95	98	100.5	111.5	4.45	„

Association and of the Boston Manufacturers' Mutual Fire Insurance Company, Professor Ordway undertook the investigation of this subject of spontaneous combustion and oils, the outcome of which is the apparatus now used in America. The apparatus consists of an outer shell formed by a 6-inch wrought iron tube, which can be closed at each end by discs of wood. Inserted into this tube is an inner 4-inch tube of sheet-iron, with overlapping metal covers at the end. Thus there is left an air space of one inch around the inner tube, and one of three inches at each end. The apparatus is conveniently placed on a tripod stand and is heated by a Bunsen burner. Three thermometers, which are inserted into the inner shell through the outer one, allow of the reading of the temperatures. •

For purposes of testing an oil, 50 grms. of the oil are evenly distributed over, say, 50 grms. of cotton waste, and the waste carefully pushed into one end of the inner tube, and one thermometer inserted into the middle of the ball. A second ball of unoiled waste is placed at the other end of the tube. On heating, the thermometer inserted into this blank waste should not rise above 100° to 101° C., which can be easily controlled by the readings of the middle thermometer. The latter should be kept at about 120° C.

The results obtained by means of this apparatus have been of the greatest use for determining the cause of fires and for gauging the degree of safety of wool oils. For instance, the percentage of fatty oil which may be safely mixed with mineral oils can be easily determined. Thus neatsfoot oil and best lard oil may be added to the extent of 50 to 60 per cent., while cotton oil should not be allowed beyond 25 per cent. •

Shavings of leather, skeins of dyed yarn, or rolls of dyed cloth may be tested in the same way in this apparatus. Paper pulp, boards, and other combustible substances, when heated to a higher temperature, would indicate the temperature at which inflammation sets in.

It may be found useful in this connection to quote the order in which the schedule of the Fire Insurance Companies in this country arranges the oils. •

Free from any extra charge are—olive and lard oils; oleine, saponified or distilled, not containing more than 10 per cent. of unsaponifiable matter; fish oil, or a manufactured oil.purified by distillation or saponification (whatever this may mean), containing not more than 30 per cent. of unsaponifiable matter, and having a flash-point of not under 340° F. (167·8° C.). A higher rate is charged for manufactured oils containing more than 30 per cent., but not more than 50 per cent. of unsaponifiable matter. A still higher rate is charged for black recovered oil containing not more than 50 per cent. of unsaponifiable matter. The highest rate is charged for manufactured oils containing more than 50 per cent. of unsaponifiable matter, or mineral oil, oil of pine, linseed oil, rape oil, cotton-seed oil, or any other seed oil.

The production of spontaneous combustion in oiled wool or cotton fibres and fabrics is governed by many factors, and the exact conditions which lead to its development in the quickest manner are not thoroughly known. The character of the oils used has some influence, as has been already pointed out. Then the proportion of oil to textile material is not without some influence; if there be either too much or too little oil, then spontaneous combustion may not occur, for in the one case the excess of oil by its cooling action will prevent the temperature from getting too high, while in the latter case the amount of oxidation is not enough to lead to such a rise in temperature as will cause the mass to inflame. The question of volume of the mass of oiled material cannot but have some influence, exactly in which direction is rather uncertain; but probably, the greater the volume the greater the risk, for there is then more surface exposed to the oxidizing action of the air on the oil than would be the case if the mass were somewhat compressed.

The presence or absence of moisture has some influence, and so far, experience shows that the presence of a small amount of moisture tends to promote spontaneous combustion rather than to retard it. Probably the moisture acts as a carrier of oxygen to the oil, or else the high specific heat of the water enables it to accumulate much heat and so specifically raise the general heat of the mass. It has been observed in the case of cotton fibres

that bales which have got damp in the process of extinguishing the fire are very liable to burst out into flames, and the only way to avoid this is to open out the bales and allow the cotton to dry.

Then the general temperature of the place where the oiled material is will have some influence, for oxidation of the oils and the heating of the wool, etc., is more likely to occur when the general temperature is high than when it is low.

Whether the spontaneous combustion breaks out first in the centre of the mass or at the outside is not known with any degree of certainty. Cases have been met with when combustion has started on the outside, while in other cases the fire has started in the centre.

The question of the flash-point, or, perhaps more strictly the firing-point, of the oil does not so much concern the production of spontaneous combustion as the extension of the fire when it has broken out. The lower the flashing- and firing-points of an oil, the more rapidly does the oil spread over the surface of bodies, because of its greater limpidity; while further the rapidity of extension of the fire is greater than with oils of high flashing- and firing-points.

It is not easy to fix a safe flashing-point having regard to the class of oils used in oiling wool, for the oleines and oleic acid have comparatively low flash-points, about 320° F., and the establishment of too high a standard would exclude these; yet a hydrocarbon oil with a flash-point of 320° F. is of comparatively low quality; good grades range from 370° to 410° F. in flash-point. The firing-point is always higher than the flash-point by from 50° to 80° F., varying in different classes of oil. An oil like olive, lard, neatsfoot, or cotton oil, if of good quality and fairly free from free fatty acid, will have a flash-point of 470° to 500° F., with a firing-point of from 550° to 600° F., so that these are, apart from the risk of spontaneous combustion, safe oils to use, for their firing-point is high, and, moreover, their spreading power is less than in the case of hydrocarbon oils. But the question of cost often precludes the use of these oils, although this extra cost may be counterbalanced by other advantages,—less liability to defective dyeing of the yarn or

cloth on which the oil is used and greater value of the recovered oil or grease from the wool.

Where price is a consideration, the best oil to use in the oiling of wool, one with which the risk of spontaneous combustion is reduced to nothing, while the firing-risk is also slight, would be a mixture of 80 per cent. of good olive, lard, neatsfoot, or earth-nut oil with 20 per cent. of hydrocarbon oil, with a flash-point of 420° F.

OLEINES.   WOOL OILS.

In addition to the natural oils, the following recovered and manufactured products are also utilized in the woollen industry :—

The term " wool oil " is applied to a variety of oils to be used in the batching of wool ; some of these, as will be more particularly specified later on, are compounded oils, others are more or less crude oleic acid, while some are products obtained in the treatment of Yorkshire grease (p. 50). To obtain the wool oils, the Yorkshire grease is subjected to distillation, which process will now be briefly described. The details of this description may not be applicable to every grease-distilling works, but will be sufficiently near to general practice for all present purposes.

The process of distillation is carried on in cast-iron stills (wrought-iron cannot be used as it is rapidly corroded by the fatty acids present in the grease), similar in shape to tar stills, and which are connected with suitable condensing arrangements.

In most works superheated steam is used as well as direct fire heat, its use giving a larger yield of more useful products, which are also of a better quality than when fire heat is used alone.

The stills are of about 1000 gallons capacity, and will hold something like four tons of grease. When beginning the distillations, fire heat is used alone until the water in the grease has been driven off, which will take ten to sixteen hours, after

which the superheated steam is run in, and kept running into the still during the rest of the distillation. •

After the water has come off, some grease gives off a small quantity of a light " spirit oil," others do not yield this product. After this comes the principal product, a thin limpid oil, or a pale yellow grease, known as " first distilled grease ". This grease•takes from twenty to twenty-four hours to come off; it is followed by a greenish oil, or " crude grease," which product is usually put back into the stills with a fresh quantity of grease, or occasionally made into very crude lubricating greases.

After about thirty-six hours from the commencement of the distillation a thick oil begins to appear, and when this occurs the fires are drawn, and the " pitch " which is left in the still is run off.

The following table shows the products and the quantities yielded :—

Quantity of grease taken—66 cwt. 3 qrs. 20 lb.

Water and loss	. .	13 cwt. 3 qrs. 16 lb. or 20·76 per cent.		
Spirit oil .	. .	2 ,, 3 ., 0 ,,	4·10	,,
First distilled grease	.	30 ,, 1 ., 26 ,,	45·54	,,
Green oil	. . .	10 ,, 1 ,, 12 ,,	15·47	,,
Pitch	. . . .	9 ,, 1 ,, 22 ,,	14·13	,,

The " first distilled grease " may be treated in two ways—(a) it may be again distilled, or (b) subjected to pressure, thus yielding two products, oleine and stearine.

(a) The first distilled grease obtained as described in the first distillation is now put back into the stills and treated as before, when two products are obtained—" second distilled grease " and " pitch ". The latter is softer than that obtained in the previous distillation, and is hence termed " soft pitch ". The principal object of this second distillation is to obtain products of a better quality and a purer colour. The first distilled grease yields about 96 per cent. of second distilled grease, and 4 per cent. of pitch.

The distilled greases obtained during the first and second distillations are collected in a tank and allowed to cool slowly, and kept at a temperature of 21° C. (70° F.)• for some hours.

By this means the stearine it contains separates out in a granular form, which facilitates the process of pressing. A great deal depends upon the careful cooling of the grease to obtain the maximum yield of oleine with the minimum amount of damage to the press cloths.

This operation of "seeding" is sometimes done in shallow metal trays placed on racks in a slightly inclined position, the racks being in a room kept at from 21° to 25° C. (70° F. to 77° F.),—the oleine which drains out of the stearine is generally considered to be of better quality than that obtained by pressure, and is commonly designated "No. 1 oil". The principal objection to this process is the rapid corrosion of the metal trays, while the metal dissolved in the oleine causes the discoloration of the latter.

The grease is now put into canvas cloths and made into cakes, which are put between the plates of a hydraulic press, where they are subjected to a pressure of about three tons to the square inch for six hours; the liquid oleine No. 2 is thus pressed out, the stearine being left behind in a solid cake. The grease yields about 66 per cent. of oleine, and 34 per cent. of stearine. The oleine is turbid as it issues from the press, and is clarified by filtering through cocoa-nut mats.

The distilled greases are of a pale-yellow colour, and are granular in structure. Two samples examined by the author had the following composition :—

	First Distilled Grease.	Second Distilled Grease.
Water	0·98	1·04
Free acid . .	63·12	66·56
Unsaponifiable matter .	12·88	13·24
Neutral oil . .	23·02	19·16
	100·00	100·00

It is interesting to note that the second distilled grease contains more free acid and unsaponifiable matter than the first distilled grease. This might be expected, since the distillation of grease must result in the partial decomposition of the neutral oils it contains, leading to the formation of acid bodies and

hydrocarbons. This is also shown in the analysis of the wool oils given below.

Oleine.—This product, which is better known as " wool oil," comes from the press as a pale-coloured body, but gradually it assumes a pale-brown colour. This coloration is undoubtedly brought about by the presence of traces of iron in the oil, derived from the metal of the press and of the tanks in which it is stored. Oleine which has been pressed and kept in glass bottles does not alter in colour.

When filtered through fine filter-cloths it is perfectly clear and transparent, but very often oleines are slightly turbid, and this turbidity is increased in cold weather. Oleine has a peculiar characteristic odour which is unmistakable

Some works only send out one quality of oleine, others make three qualities : No. 1, drained from the second distilled grease ; No. 2, pressed from the same ; and No. 3, pressed from first distilled grease.

These oils are mostly used for oiling wool, hence their name. They have been used for making lubricating greases and for soap-making, but do not answer satisfactorily for the latter purpose.

Oleines, even from the same maker, vary very much in composition, which depends, as might be expected, on the composition of the grease from which they are distilled.

The following table contains some analyses of several samples of wool oils :—

	1.	2.	3.	4.	5.
Spec. grav. at 15·5° C.	0·9031	0·898	0·905	0·9000	0·9091
„ „ 98° C.	0·852	0·8403	0·849	0·8431	...
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Water	1·12	2·33	1·38	2·51	...
Free acid	55·02	56·26	53·65	59·83	64·42
Unsaponifiable matter	34·66	29·46	16·32	38·92	9·95
Neutral oil	9·20	11·95	28·65	...	25·63
	100·00	100·00	100·00	101·26	100·00

These figures can only be taken as approximately correct ; the free acid is calculated as oleic acid, while probably there are

other acids present, both of higher and lower combining weights. Nos. 1, 2, and 3 oils in the above table are analyses of the three qualities of oil previously noted.

Some people consider that the presence of the unsaponifiable matter indicates adulteration with mineral oil. Such a mixture would be very difficult of detection, and one would have to pay more attention to the physical rather than the chemical properties of the oil obtained after saponification and separation of the neutral oil and fatty acid present in the wool oil.

The flashing-points of the three qualities of wool oil are given in the following table :—

	No. 1 Oil.	No. 2 Oil.	No. 3 Oil.
Vapourising temperature .	212° F.	203° F.	172° F.
Flashing-point . . .	338° F.	342° F.	322° F.
Burning-point	386° F.	397° F.	356° F.

It would be advisable to reject any oil that has a lower flashing-point than 330° F. for oiling wool.

Wool grease oleine has a distinct optical activity, ranging, according to Marcusson (" Mitt. Konigl. Materialprufungsamt." 1910, 469) from [a] $_d$ = + 10° to + 19°. It is also usually soluble in its own volume, or one and a half times its volume of 96 per cent. alcohol, at 20° C., and these two tests furnish useful means of detecting the presence of mineral oil in any considerable quantity.

Another test for the presence of mineral oils, which also detects refined rosin oil, has been proposed by Winderfield and Mecklenburg (" Mitt. Konigl. Materialprufungsamt." 1910, 471). It consists in treating the sample with an equal volume of a mixture of 90 per cent. methyl alcohol, and 10 per cent ordinary alcohol, when a pure oleine usually gives a clear solution at 20° C., but samples containing 10 per cent., or in most cases 5 per cent of mineral oil, give a turbidity and gradual separation of an oily layer.

The wool oils or oleines obtained by distillation from crude wool greases as just described are distinguished from other wool cleines by containing cholesterine or cholesterol, and this can be detected by the following colour-tests :—

About $\frac{1}{2}$ a gramme of the oleine is taken and mixed with 2 c.c. of chloroform and 2 c.c. of sulphuric acid, and the mixture well shaken. The chloroform layer is coloured blood-red to purple from the presence of cholesterine, while the sulphuric acid layer has a strong green fluorescence. The addition of more chloroform to the mixture causes it to turn blue. A similar test is to add to the chloroform solution 20 drops of acetic anhydride, and then one or two drops of concentrated sulphuric acid, when a violet-pink coloration is obtained.

Many oleines, both those from wool grease, and oleic acid, are sold by the makers of certain specified qualities as containing 60 per cent., 70 per cent., 80 per cent., up to 98 per cent., etc., of saponifiable matter, consisting of all free oleic acid and any unchanged neutral oil.

An examination of these products for free acid, unsaponifiable. matter, etc., is carried out in the manner detailed in the chapter on " Oil Analysis."

OLEIC ACID.

Oleic Acid is a bye-product in the manufacture of stearic acid and palmitic acid from tallow and palm-oil for candle-making. There are four processes employed in this industry for the separation of the fatty acids from glycerine, viz. :—

(1) The "Autoclave" or Lime Saponification Method.

(2) The "Distillation" or Sulphuric Acid Process.

(3) Twitchell's Process.

(4) The Castor-seed Ferment, or Enzyme Process.

1. **The Autoclave Method.**—The autoclave is a strong cylindrical iron or copper vessel, capable of standing a considerable pressure. Into the autoclave is placed a mixture of the oil or fat with an equal quantity of water, and about 3 per cent. of lime, and the mixture is subjected to the action of steam at 200 to 250 lb. per sq. in. for 8 to 10 hrs. Decomposition of the fatty material results, an aqueous solution of glycerine, some lime soap, and free fatty acids being produced. The aqueous solution is run off and used for the preparation of glycerine; the mixture of lime soap and fatty matter is collected, treated

with hydrochloric acid, which decomposes the lime soap and liberates the fatty acids it contains. The whole mass of fatty acids is collected and dealt with as hereafter described.

The oleine (oleic acid) and the stearine (stearic or palmitic acid) are often commercially designated as " saponified stearines," etc., in contradistinction to those obtained by the distillation process.

2. **The Distillation Method.**—This is carried out in the following manner : the fats or oils are melted and then mixed with a small proportion (3 to 6 per cent.) of sulphuric acid ; the mixture is next placed in a still and distilled, a current of superheated steam passing through the still ; there distils over water containing glycerine and fatty acid,—the former is used for making refined glycerine, the latter is dealt with as described below. The oleine (oleic acid) and stearine (stearic or palmitic acid) obtained in this process are commercially designated as " Distilled stearines " or " oleines." This method of treatment is only suitable for the decomposition or hydrolysis of very low grade materials, as there is considerable loss of glycerine. The mixed fatty acids obtained by this method contain more solid fatty acids (stearine) than those resulting from the "lime saponification."

3. **Twitchell's Process.**—In this process the fat or oil is treated with steam in the presence of $\frac{1}{2}$ to 2 per cent. of naphthalene stearosulphonic acid ('Twitchell's Reagent), after a preliminary boil with 1 to 2 per cent. sulphuric acid of 60° B. After 24 to 36 hours most of the oil is resolved into fatty acids and glycerine.

.4. **Castor-seed Process.**—By this process the hydrolytic power of the enzyme present in castor-seeds is made use of to separate fatty acids from glycerine. The fat or oil is mixed with about one-third its volume of water, and 7 to 10 per cent. of a specially prepared castor-seed extract added, together with about 0·2 per cent. of manganese sulphate. The mixture is thoroughly emulsified by blowing air through it, and maintained at a temperature of 25° to 40° C. according to the nature of the oils, but about 2° to 3° higher than their solidifying point, for

about 48 hours, when on warming to 80° to 85° C., and allowing to settle, the fatty acids rise to the surface, leaving the glycerine in the aqueous portion underneath.

The mass of fatty acid obtained by any of these processes varies in composition according to the character of the oil or fat used. Thus if tallow has been used, it will consist of a mixture of oleic acid, palmitic acid, and stearic acid ; if palm oil has been used, of a mixture of oleic acid and palmitic acid, and so on with other oils.

Virtually the manufacturer simply regards it as being composed of two products only : one liquid, chiefly oleic acid, which he calls "oleine"; the other solid, which he calls "stearine". To separate these two products he maintains the acids at a moderate heat (100° F.) for some time, when the stearine separates out in grains. The granular mass is placed in stout canvas bags and subjected to hydraulic pressure, when the oleine flows out, leaving the stearine behind.

The oleine or oleic acid is sold to wool manufacturers for oiling wool, and is also used for a variety of other purposes. The stearine need not be considered further.

Oleic Acid, Oleine, Cloth Oil.—The oleic acid so obtained is sold under a variety of names—"oleic acid," "oleine," "brown cloth oil," "brown wool oil," etc., etc., in some cases just as it comes from the press, in others blended with other oils.

It may vary in colour from a pale straw—when it is known particularly as "pale oleine" or "pale oleic acid," and is the article that should be used on the best wool—to a reddish-brown liquid of various hues, having a sharp and somewhat characteristic odour. The specific gravity varies from 0·898 to 0·905 at 60° F. The proportion of actual acidity calculated as oleic acid, may vary from 84 to 97 per cent. There is almost invariably some unchanged oil, usually varying in quantity from 2 to perhaps 10 per cent., and larger quantities have been recorded. There are also small quantities of unsaponifiable bodies of a hydrocarbon nature which are, so to speak, natural to the product, and have been produced by decomposition of the fat during the process of saponification or distillation ; these vary in

amount from 0·6 to 5 per cent., being perhaps greater in distilled oleines than in saponified oleines. The following table shows the analysis of several commercial oleic acids :—

	Pale Oleic Acid.	Brown Oleic Acid.	Brown Cloth Oil.	Brown Cloth Oil.	Cloth Oil.
Colour . . .	Straw.	Pale brown.	Brown.	Brown.	Dark brown.
Specific gravity . .	0·904	0·899	0·901	0·902	0·903
Free acid . . .	97·8	96·3	93·8	89·4	92·2
Unsaponifiable oil .	1·0	1·3	3·9	2·0	3·2
Free oil . . .	1·2	2·5	2·3	8·6	5·6

BLENDED WOOL OILS.

Besides the simple oils and oleines described in previous sections, which are certainly the best to use, especially in view of the recovery of the oil after use and the better value of the recovered grease, various blended wool oils are frequently sold. The composition of these is very various, but practically they are compounded of :—

1. Animal and vegetable oils,
2. Oleines, i.e. oleic acid, etc.,
3. Hydrocarbon oils,

the exact composition being largely dependent on the price at which it is to be sold. The first class of oils is the most expensive, the last class the cheapest, and the cheaper the oil the more of this class must be present.

Viewed simply as lubricants for wool, hydrocarbon oils are efficient enough; their presence reduces the risk of spontaneous combustion of oiled wool, but it is generally considered by insurance companies that the fire risk in another direction is increased, as these oils spread more easily than fatty oils and are more readily inflammable. To some extent the flash-point is a measure of degree of inflammability, and this should not be below 320° F.

Oils which contain large proportions of hydrocarbon oils are not so readily scoured out of the wool on account of the unsaponifiable nature of the hydrocarbon oils, and so the dyeing properties of the wool are reduced or deteriorated, and there

is more liability for the colour of the dyed fabric to come up un-level or uneven in patches of dark and light places.

Further, the grease recovered after using such oils contains much more unsaponifiable matter, and is less valuable in con-sequence.

In the chapter on " Oil Analysis " will be found details of methods for determination of specific gravity, saponifiable oil, free acid, and unsaponifiable oil, in such blended wool oils.

There have been used what may be termed " emulsified wool oils," or mixtures of a variety of ingredients—brown .grease, oleines, hydrocarbon oils, with water and an alkali. The only good feature about these is their low price, otherwise they are rather unsatisfactory in many respects. They are now .used only to a very limited extent, if at all.

OILS FOR COTTON-DYEING, PRINTING, AND FINISHING.

In the colouring by dyeing or printing of cotton fabrics, and in the process of finishing thereof, there are used various oils and oily preparations for various objects or purposes, without, however, any general feature connecting these one with another.

COLOUR OIL.

Oil has been added to the printing pastes—" colour," as they are technically called—of the calico printer for a long period. This oil has, in most cases, only one purpose to serve, that of preventing frothing, which happens in many cases owing to the starch, British gum, gum tragacanth, or albumen which has been added as a thickening agent to the colour, or to tannic acid added with some colours as a mordant for the dyestuff which is employed. Such frothing, if it occurs, leads to poor, thin, and uneven effects being printed on the cloth.

In some other cases, more particularly with what are called " mordant colours "—alizarine, logwood, Persian berries, alizarine blue, etc.—the oil not only prevents frothing, but it may enter into combination with the dyestuff and lead to fuller and brighter colour effects being obtained.

Olive oil has long been the standard oil for this purpose, and

it certainly does its work effectually in every way.   Olive oil
has already been ʼdescribed in pp. 88 *et seq*.

Of late years several preparations under the general denom-
ination of " colour oil " have been offered to calico printers.   For
these there is no standard composition.   The best of them are
mixtures of a hydrocarbon oil and either olive or rape oil;
some consist of hydrocarbon oils only.   The following are
typical examples :—

<div align="center">

1.

70 parts 890 Scotch oil.
15   ,,   885 American oil.
15   ,,   olive oil.

2.

80 parts pale 865 American oil.
10   ,,   Russian spindle oil.
10   ,,   rape oil.

3.

80 parts pale 865 American oil.
20   ,,   Russian spindle oil.

</div>

Where price is not a great element, and it is desired to use
an oil that shall not tint the printing colour or the cloth in any
way, white petroleum oils may be used with advantage.

These blended colour oils are found to prevent frothing very
well.   The quantity used is not large, varying from 2 to 5 per
cent. of the weight of the printing colour.

TURKEY-RED OILS.

In the dyeing and printing of Turkey and alizarine reds on
cotton, the dyeing and printing of paranitraniline red and
similar developed colours on cotton, in the printing of various
colours with such mordant dyes as alizarine, alizarine cyanine,
alizarine yellows, chrome yellow, gallocyanine, etc., oil is used
as an essential constituent of the process, although it is not yet
definitely known what part the oil plays in the production of
the finished colour; but it is a well-recognized fact that when
oil is used, fuller, brighter, and faster colours are obtained than
when oil is not used.

In past times olive oil, more particularly that variety known

as "Gallipoli oil" in England and "*huile tournante*" in France, which is of rather poor quality and contains much free fatty acid (the author has found 20 per cent. in some samples), was almost solely used for this purpose.

In use the oil is mixed with water and a little soda, when an emulsion is formed in which the cotton is worked. The presence of free fatty acid in the oil enables this emulsion to form more readily and be more permanent in character than if it were absent, for it combines with the soda to form a soap. It is necessary in order to obtain the best results, that the emulsion should contain free oil and some free fatty acid as well as soap. Soap will not answer the purpose, and only enough is produced to give a good emulsion, as then the cotton becomes more evenly impregnated with the oil, and therefore more level and uniform shades are obtained.

John Mercer introduced and patented in 1846 the use of sulphated [1] olive oil prepared by the action of sulphuric acid on olive oil (see below), which being soluble in water, gave better results. John Mercer's discovery remained in abeyance or was not employed by the great bulk of calico printers and dyers for many years, but about 1870 to 1875 there came into use sulphated castor oil, and this has now quite superseded olive oil in the production of Turkey and alizarine reds and other colours on cotton. It is made and sold under a variety of names. Turkey-red oil or alizarine oil are the most general, then oleine, soluble oil, dyeing oil, red oil, etc. The method of preparing this product will be described presently. It may be mentioned here that as commonly sold it is an oily liquid, mixing readily with water, and containing on an average 50 per cent. oil, 1 per cent. alkali, 1 to 2 per cent. salt, and 48 per cent. water. Some makes contain up to 75 per cent. oil, and the particular variety sold as soluble oil often contains only 25 per cent. of oil. As the oil is the most valuable part of the product, it ought to be bought to contain a definite quantity of oil and the price regulated accordingly.

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[1] The term "sulphonation" has been frequently applied to this treatment, but it is preferable to use the terms "sulphation" and "sulphated".

This sulphated castor oil is not difficult to make, and many users, especially those calico printers and dyers employing a chemist, make it themselves. When purchased from makers, buyers would find it better to buy the higher strengths and so save in cost of freight.

TURKEY-RED OIL. ALIZARINE OIL. OLEINE.

There is used in the dyeing and calico-printing trades, under the above names, a preparation of castor oil which is of comparatively modern introduction. Its use has been found to materially increase the brilliancy of Turkey reds, alizarine reds, and many printed colours, while in recent years its use in connection with direct dyes like Congo red, benzopurpurine, etc., has been found advantageous in the direction of producing more level and uniform shades on unbleached cotton. In the Holliday process of producing colours direct on cotton, as, for instance, the well-known Para reds, and alpha clarets, the use of Turkey-red oil seems necessary if bright and fast colours are to be produced.

John Mercer's patent for the preparation of sulphated olive oil is as follows :—

" The first part of our invention consists in preparing what we call 'sulphated oil,' and applying the same to the processes herein mentioned. For this purpose we take at the rate of one part by measure of sulphuric acid of commerce for every eight measures of olive oil; we mix the same, and stir them frequently during ten days; we then add three or four gallons of water, stir the mixture well, adding three or four pounds of common salt, and then allow the whole to stand; the oil will separate, and may be drawn off clear. This, for convenience of description, we will call 'sulphated oil A '. For each gallon of this oil, we take nine gallons of solution of hypochlorite of soda, which we prepare in the following manner :—

" We take sixteen pounds of crystallized carbonate of soda of commerce, dissolved in two quarts of water and ten gallons of chloride of lime (bleaching powder) liquor at 12° Tw. ; we mix these materials well together, and after allowing the same to

stand, we draw off the clear liquor, which we employ as above
mentioned. We heat the mixture of sulphated oil A and hypo-
chlorite of soda by any convenient means, preferring a pipe
heated by steam, and boil the mixture until the same ceases to
bleach a piece of cotton dyed of a pale blue colour by indigo.
Or, in place of applying heat, we use a diluted acid (preferring
sulphuric diluted in the proportion of one measure of concen-
trated acid to twenty-four measures of water), and we add and
stir in the diluted acid in portions at intervals, allowing time
to prevent as much as possible the escape of free chlorine ; and
when the mixture no longer bleaches a piece of cotton dyed
light blue by indigo, the process will be complete. Or we treat
the sulphated oil A with atmospheric air and steam, for which
purpose we mix at the rate of one gallon of the oil with one
gallon of water, and force streams of heated atmospheric air
through a suitably perforated pipe or other suitable apparatus,
such as are well understood and have before been used when
applying streams of heated air or steam to fluids for other
purposes. We prefer that the air should be heated to 220° F.,
and keep up the process for ten days. We find that the process
is quickened by adding one gallon of cow-dung water and one
gallon of bran water made with two pounds of bran ; or, instead
thereof, one-eighth of a gallon of linseed oil ; or we use eight
ounces of common salt. When using cold atmospheric air we
employ steam by perforated tube, so that the agitation of the
surface favours the action of the atmosphere on the oil; but
this process of oxidation is slow when compared with forcing
heated air through the oil, or when compared with causing
streams of steam and cold air alternately to pass through the
oil. The oil, instead of being first sulphated as above explained,
may be treated in the same manner, and we find it desirable to
prepare both sulphated oil and oil without that process, as above
explained, and we use them as hereinafter described. The first
we call 'sulphated oxidized oil,' and the others we call 'oxi-
dized oil'.

"Another mode of manufacturing sulphated oxidized oil,
according to our invention, is as follows : We mix at the rate

of one part by measure of strong sulphuric acid with eight measures of olive oil, and stir the mixture often during twenty-four hours; to this mixture we add at intervals twenty ounces of chlorate of potash, dissolved in two quarts of boiling water, to each gallon of oil, and stir until the action ceases. We then wash away the acids and salts by water, by stirring in two gallons of water for each gallon of oil; then allow them to stand, and draw off the water, and repeat the washing in the same manner with two more gallons of water. Or (instead of the chlorate of potash above mentioned) we employ forty ounces of bichromate of potash dissolved in five pints of water, and proceed in the same manner as before described. Or, in place of the above we employ forty ounces of nitrate of soda, or of potash, in the state of powder, and one pint of water, and proceed in the manner above described. By either of the above processes we obtain a preparation of sulphated oxidized oil; and having prepared the oil as above described, and two quarts of oxidized oil, to these we add twelve gallons of pearl-ash liquor of 2° Tw. The goods or fabrics are to be impregnated with this oil liquor four times, and dried after each time in a hot flue or stove. The goods or fabrics are then to be impregnated twice with pearl-ash liquor of 6° Tw., and dried in a hot stove or flue after each time of impregnating, then finishing at the temperature of 180° F. for upwards of three hours; the goods or fabrics are then to be rinsed in pearl-ash liquor of 1° Tw., then washed, and afterwards dried at about 140° F.; the goods are then ready for the usual mordants and after processes, as well understood"

John Mercer used olive oil for making his sulphated oil, but practical experience has since shown that castor oil gives by far the best results. The action of the sulphuric acid goes on more regularly and smoothly, there is not the same amount of the charring action which, in the case of olive oil, causes loss of material as well as discoloration of the final product. If charring does occur, it is due to faulty manipulation, as, for instance, running the acid into the oil in too large a quantity at once, when a considerable rise of temperature takes place, or using too large a quantity of sulphuric acid. It has been

attempted to use sulphated cotton and corn oils, which are cheaper than castor oil, but they have been found unsuitable. The action of the acid on these oils is too energetic, and dark-coloured products are the result. Sometimes small quantities of other oils, as, for instance, olive, cotton, maize, mineral, or rosin oil, are added to the castor oil to produce a cheaper product, but the results are not good.

While in the main the makers of these oils all follow the same general plan, yet there may be small differences between them in carrying the operation out, such as using different proportions of oil and acid, varying methods of mixing them together, varying times of settlement and modes of washing the acidified oil and neutralizing it afterwards.

The process of manufacture is comparatively simple, and requires no elaborate plant. A wooden tank or barrel of a suitable size, according to the quantity of oil which is to be made, is necessary. This should be of a capacity of from two and a half to three times the volume of the oil to be treated; thus if 40 gallons of oil are to be dealt with, a tank of at least 100 gallons would be provided, for practically the quantity of the finished product will be twice that of the oil started with. There are required also tanks or vessels to hold the solution of caustic soda or ammonia used, with suitable measuring vessels and test glasses. The vat or barrel in which the preparation is made should have a tap fitted in the bottom end for running-off purposes, and if the bottom be slightly inclined to the tap, so much the better. It is a good plan to have a gauge fitted to it, in order to be able to measure the quantity of liquid in the vat or barrel at any time.

The following is a general description of the process; by using it with the quantities given a very good product is obtained :—

40 gallons of castor oil of fairly good quality are run into the vat; 80 lb. of strong sulphuric acid 66° B. are then weighed out, and run into the oil in a thin stream, or in small quantities at a time, stirring well into the oil and maintaining the tempera-ture at 36° to 40° C. The whole operation ought to take at least

an hour, and after all the acid has been run in, the stirring should be kept up for half an hour so as to ensure that the oil and acid are well mixed together. The mixture is now left at rest for a period of not less than twenty-four hours, or for longer if more convenient.

After this standing there is added to the oil mass 40 gallons of water, which is well stirred in until a uniform mixture of a creamy colour without any dark streaks is obtained. Too much attention cannot be given to the effectual mixing of this water with the oil mass. The whole is now again left to stand for not less than twenty-four hours, indeed a little longer period is advisable. In winter thirty-six hours will be required. At the end of this time the mass will have separated into two layers, one of oil at the top, the other of an aqueous acid layer at the bottom. This latter is run off by means of the tap which has been fixed at the bottom of the vessel.

It is at this point in the process that makers often vary in their methods, some finish it off at this point, others give the oil a second washing, using this time a strong solution of common salt containing 1 to $1\frac{1}{2}$ lb. salt per gallon or a solution of Glauber's salt, working this in the same manner as the first washing—the idea being to eliminate as much of the sulphuric acid as possible. There is no great advantage in this treatment.

There is now prepared a solution of caustic soda of 40° Tw. strength. This solution is poured into the acidified oil slowly and with constant stirring; at first a creamy mass is formed, then dark streaks will show themselves, increasing in number as the caustic solution is poured in; finally the whole mass of liquid will become clear and transparent, when the addition of the soda solution is stopped. Usually about 10 gallons of the caustic soda liquor will be required, but the proportion will vary from time to time on account of varying degrees of action of the acid on the oil, due to differences of temperature, rate of mixture, time of standing, amount of washing, etc. The preparation of the oil is finished by adding enough water to bring up the volume to '75 gallons. If the addition of the water

makes, the oil milky in appearance, the addition of a little more soda solution will restore the transparency. •

Some makers use both caustic soda and ammonia in preparing their Turkey-red oils. In this case about three-fourths of the amount of caustic soda required for complete neutralization is first added, and then a mixture of 1 gallon liquid ammonia with 1 gallon of water is added until complete neutralization is effected. •

If sufficient water is not added in the first washing, or sufficient time is not allowed for settling, there is a liability for an excess of sulphuric acid to be left in the oil. This forms sodium sulphate with the caustic soda, the presence of which gives rise to two faults—first, the oil is turbid in appearance; and, second, there is a tendency for the oil to separate into two layers, one of watery liquid at the bottom, the other of clear oil at the top. This latter separation is also liable to occur if sufficient caustic soda to neutralize the acidity of the oil has not been used, so that the oil is left on the acid side.

The use of ammonia for neutralization has certain advantages, especially in the finishing and printing of steam colours, because the alkali volatilizes and leaves only the free fatty acid on the cloth.

The reason why castor oil is the most suitable for Turkey-red dyeing is because it has the property of forming a soluble soap with a minimum proportion of alkali. Solutions of other fatty oils give emulsions rather than clear solutions, when the proportion of alkali falls much below that required for complete neutralization. Again, the decomposition of the oil by the action of sulphuric acid is more complete with castor oil than with any other oil which can be used, and maximum decomposition is essential to the achievement of the best results. A certain proportion of undecomposed oil has, however, the advantage that it lessens the tendency to frothing, and the decomposition by means of sulphuric acid in the case of castor oil provides for the ready attainment of this condition.

The proportion of sulphuric acid to castor oil used in making the oil has an influence in determining the quantity of caustic

soda required to neutralize the resulting acidified oil, and on the solubility of the finished product. To make a good, clear, and fairly soluble oil, not less than one part of acid should be used to five parts of oil—that is, 20 per cent. of acid, as in the process detailed above. When only 10 per cent. of acid is used, only 21 per cent. of the alkali solution is required for neutralization, and the mixture, after standing some time, sets to a solid, which does not freely dissolve in water, and only forms a very milky liquid. When 15 per cent. of acid is employed, a soluble oil is produced, but this forms a milky emulsion with water, and does not clear. When 25 per cent. of acid is used, then the acidified oil takes 30 to 32 per cent. of the caustic soda solution to neutralize it, and gives an oil which is freely soluble in water. The use of too great an excess of acid should be avoided, for it increases the quantity of soda required, while the acidified oil becomes more freely soluble in water, and there is then a greater risk of some of the oil passing away in the wash-waters, and so being lost.

Commercial Turkey-red oil, alizarine oil, or oleine is a fairly limpid fluid, rather more viscid than water, but less so than castor oil ; in colour it resembles the latter liquid, and its odour is characteristic. It mixes freely with water in all proportions, giving slightly opalescent solutions, the clearness or transparency of which depends entirely upon the degree of alkalinity of the oil. The specific gravity is rather more than that of water, and depends on the strength. A sample having a specific gravity of 1·0294 contained—

48·44 per cent.	water,	
1·49	,,	sodium,
47·59	,,	fatty matter,
2·48	,,	sodium sulphate,

while a sample having a specific gravity of 1·040 contained 44·5 per cent. fatty matter.

The chemical composition of this peculiar oily product has been the subject of investigation at the hands of many chemists, whose results and conclusions differ somewhat one from the other; this is what might naturally be expected, because there

are many factors operating during its preparation which will cause it to vary. Strength of acid, ratio of acid to oil, length of time of action, temperature, and mass, will be found to vary from time to time, and will all have some influence in affecting the composition of the final product. Many of the views enunciated by those who have considered this question are of a speculative character, for the difficulties of research as to the constitution of Turkey-red oil are very great.

The fatty matter of this oil is certainly present in three forms —first, as unchanged oil, which is not soluble in water, but is readily emulsified; second, as free fatty acid; and third, as sulphonated or sulphated fatty acids,—and it is largely as to the nature of these that observers differ from one another.

A brief résumé of the principal opinions expressed by those chemists who have given attention to the matter will be of interest. It is perhaps only fair to emphasize the fact that, although nominally they have been working on the same oil, yet, owing to the factors of variation mentioned above, the actual products may have been really different.

Liechti and Suida were among the earliest chemists to express any opinion on this subject. They regard the soluble part of Turkey-red oil to be glycerol sulphates, which, if the oil has been made from olive oil, will be partly derived from hydroxyoleic acid and partly from hydroxystearic acid. The former has the formula—

$$\left.\begin{array}{cc} C_{18}H_{33}O_3 & C_3H_5OH \\ SO_4 & \\ C_{18}H_{33}O_3 & C_3H_5OH \end{array}\right\} \text{ hydroxyoleic, glyceryl sulphate,}$$

the latter is

$$\left.\begin{array}{cc} C_{18}H_{35}O_3 & C_3H_5OH \\ SO_4 & \\ C_{18}H_{35}O_3 & C_3H_5OH \end{array}\right\} \text{ hydroxystearic, glyceryl sulphate.}$$
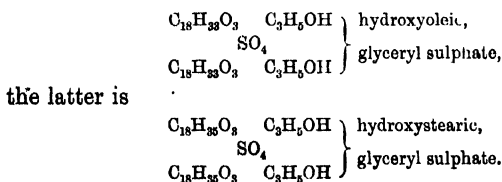
More recent work has thrown some doubt on this point, partly because these must yield glycerine on saponification, and there is little glycerine in Turkey-red oil.

Müller Jacobs considers that the action of sulphuric acid is a sulphating action, that is, there is introduced the group, HSO_3, and thereby the fatty acid is rendered soluble in water.

Thus the principal constituent of an olive-oil product would be hydroxystearin sulphonic acid, $C_{17}H_{33}OH$, SO_3H, $COOH$, while that in a castor-oil product would be $C_{17}H_{31}OH$, SO_3H, $COOH$ hydroxyolein sulphonic acid.

Benedict considers the products to be sulphuric ethers, whose constitution is shown in the formulæ $C_{17}H_{34}O$, SO_3H, $COOH$ hydroxystearin sulphuric ether, or $C_{17}H_{32}O$, SO_3H, $COOH$ hydroxyolein sulphuric ether. By boiling with strong hydrochloric acid, these products are decomposed into sulphuric acid and hydroxystearic or hydroxyoleic acids.

Juillard, who has made some rather extensive researches on this oil, has come to the conclusion that one result of the action of the sulphuric acid is polymerisation of the ricinoleic acid of the castor oil, and that di-, tri-, tetra- and penta-ricinoleic acids are formed, and that these are combined with the sulphuric acid. Scheurer-Kestner also agrees with Juillard as to the formation of the polymer diricinoleic acid but considers that the higher polymers were produced by secondary reactions. Besides these polymers Juillard has isolated other bodies, and he gives the following list of acid bodies, etc., present in Turkey-red oil made from castor oil.

The different products formed by the action of sulphuric acid on ricinolein are as follows:—

1. Ricinoleic sulphuric acid, $OHSO_2O.C H_{32}CO_2H$, is a dibasic acid, stable only in dilute solution, concentrated solutions readily decomposing into sulphuric acid and ricinoleic acid. It has the characteristic property of forming acid salts when treated with solutions of almost any salt, e.g. on agitating its solution with potassium chloride, acid potassium "ricino-sulphate," and HCl result. The corresponding sodium salt was formerly erroneously described as diricinolein sulphuric anhydride.

2. Dihydroxystearo-sulphuric acid—

$$OHSO_2O$$
$$\diagdown$$
$$C_{17}H_{33}CO_2H,$$
$$\diagup$$
$$OH$$
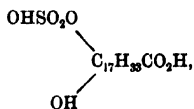
almost always accompanies 1, and possesses similar properties.

3. Dibasic diricinoleic acid—

$$O<\frac{C_{17}H_{32}CO_2H.}{C_{17}H_{32}CO_2H.}$$
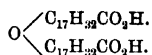
A thick liquid, soluble in alcohol. Its methyl and ethyl salts, however, are almost insoluble in alcohol, and on this property is based a method of separation of this from other acids particularly from isoricinoleic acid. It is very stable, and is not saponified by boiling alkalis.

4. Monobasic diricinoleic acid—

$$OHC_{17}H_{32}CO_2C_{17}H_{32}CO_2H.$$
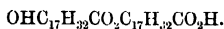
This is the first member of the series of polyricinoleic acids having the general formula—

$$OH(C_{17}H_{32}CO_2)nC_{17}H_{32}CO_2H.$$
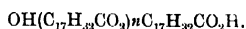
When castor oil is treated with sulphuric acid in the proportions of one part acid (98 per cent.) to eight parts of castor oil, the product consists almost entirely of these polyricinoleic acids, while with a larger proportion of sulphuric acid, isoricinoleic and dibasic diricinoleic acids chiefly result.

5. Dioxystearic acid—

$$C_{18}H_{36}O_4.$$

It melts at 66° to 68° C., and is very soluble in alcohol and ether.

6. A solid acid which melts at 70° C., and is soluble in alcohol and ether, answers to the formula $C_{36}H_{70}O_7$ and appears to be a molecular compound of dihydroxystearic and ricinoleic acids.

7. Isoricinoleic acid, $C_{18}H_{34}O_3$. An oily liquid, soluble in alcohol and ether. It is distinguished from ricinoleic acid by its solubility in petroleum ether, and appears to be a ketonic acid with formula—

$$CH_3(CH_2)_5CH_2COCH_2(CH_2)_8CO_2H,$$

or perhaps—

$$CH_3(CH_2)_5COCH_2CH_2(CH_2)_8CO_2H.$$
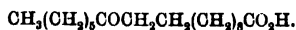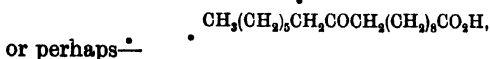
With respect to the product from olive oil, it is considered

that at temperatures of from 0° to 5°, the initial action of sulphuric acid on this oil is to form direct addition compounds, namely, dioleinhydroxystearin-monosulphuric and monoleindihydroxystearin-disulphuric esters.

$$\left.\begin{array}{c} HSO_4C_{17}H_{34}COO \\ (C_{17}H_{33}COO)_2 \end{array}\right\} C_3H_5$$

and—

$$\left.\begin{array}{c} (HSO_4C_{17}H_{34}COO)_2 \\ C_{17}H_{33}COO \end{array}\right\} C_3H_5$$
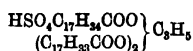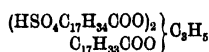
These, by further action of the acid, are respectively resolved into—

$$\left.\begin{array}{c} C_{17}H_{33}COOC_{17}H_{34}COO \\ C_{17}H_{33}COO \end{array}\right\} C_3H_5SO_4H$$

and—

$$\left.\begin{array}{c} C_{17}H_{33}COOC_{17}H_{34}COO \\ HSO_4C_{17}H_{34}COO \end{array}\right\} C_3H_5SO_4H$$
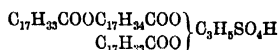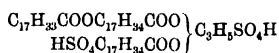
The sodium salts of the latter compounds together with their derivatives, and products of decomposition—namely, oleic, hydroxystearic, oleostearic, and possibly oleohydroxyoleic acids —constitute the oil-magma which is produced by the prolonged action of sulphuric acid on olive oil, after it has been freed from uncombined sulphuric acid by washing successively with sodium sulphate and sodium chloride solutions, the glycerine sulphuric esters decomposing the alkaline salts, and thus becoming neutralized. When boiled with dilute hydrochloric or sulphuric acid, the sulphuric acid is completely eliminated from this magma, and a mixture of oleic, oleostearic, hydroxystearic, and, perhaps, oleohydroxyoleic acids is produced.

It is thought that the value of Turkey-red oil for dyeing purposes depends upon the proportion of the soluble sulphated acids it contains, but at present no attempt is made, commercially, to buy Turkey-red oil on the basis of the amount of such acids it contains; indeed it is doubtful whether a maker could regulate the formation of these acids with sufficient accuracy to guarantee any fixed amount, as so much depends on the proportion of sulphuric acid used, its strength, temperature, conditions of mixture, all of which factors may vary from time to time.

The presence of glycerol in ordinary Turkey-red oil is certain, but it is not an essential feature of the oil, for oil of identical properties can be prepared from the mixed acids obtainable by saponifying castor oil with caustic soda and separating out the fatty acids by addition of sulphuric acid, or from the similar acids of olive oil obtained in the same way.

From a tinctorial point of view, Scheurer-Kestner has noticed that it is the sulphated fatty acid which tends to produce yellow shades of Turkey-red from alizarine, while the polymerized fatty acids are favourable to the blue shades.

The solubility of Turkey-red oil in water is due to the presence of sulphated acid, while the fluorescence always exhibited is due to the non-sulphated but polymerized acids, which have a molecular weight of 472 as against 402 given by the sulphated fatty acids obtained in the same experiment. (The molecular weight of the normal acid is 298.) Sulpho-ricinoleic acid, as precipitated from aqueous solution by sodium sulphate, forms a syrupy hydrate, and constitutes about 40 to 50 per cent. of the most soluble kind of Turkey-red oil.

Turkey-red oil may be separated into two distinct portions by dissolving it in ether, washing the ethereal extract with brine until the washings are free from sulphuric acid, and then shaking with water. The water extracts one part believed to consist of ricinoleo-sulphuric acid, while the remainder retained by the ether is considered to be free ricinoleic acid together with a small amount of neutral oil. The sulphated fatty acid may be separated from the aqueous solution by salting out with a solution of sodium sulphate. The relative proportions of the water-soluble and ether-soluble constituents varies even when the oil is produced under apparently identical conditions.

The composition of Turkey-red oil, as used in finishing in the Bradford district, has been recently very fully examined by Richardson and Walton ("Journ. Soc. Chem. Ind.," 1912, p. 105). They found the sample to contain 19·13 per cent. of sodium salts of sulphated fatty acids, 22·71 per cent. of free fatty acids and their salts, and 3·43 per cent. of neutral oil. The sodium salts of the sulphated fatty acids consist of 14·73 per cent. sodium salt

of ricinoleic acid sodium sulphate, and 4·40 per cent. mono-glyceride of ricinoléic sodium sulphate ; the free fatty acids con-tain ricinoricinoleic acid 3·33 per cent., ricinoleic acid 8·91 per cent., 'and sodium ricinoleate 10·47 per cent., and the neutral oil is made up of diricinolein 4·21 per cent., triricinolein 1·05 per cent., unsaponifiable matter (phytosterol) 0·17 per cent.

These authors confirm Scheurer-Kestner's opinion that the polymerisation of the fatty acids does not exceed that of the di-compound, i.e. ricinoricinoleic acid, $HO.C_{17}H_{32}CO.OC_{17}H_{32}COOH$, the molecular weight of which is 578·53.

Oxy-Turkey-Red Oils.

Schmitz & Toenges, of Heerdt, near Dusseldorf, in Rhenish Prussia, make a class of Turkey-red oils which they call "oxy-oleates ". To prepare these, castor oil or olive oil is sulphated in the ordinary manner with sulphuric acid ; the oil is washed with water and brine, then heated in open vessels to from 105° to 120° C., by which means the sulphur is eliminated from the oil. The next proceeding is to neutralize with alkali. They are said to be more advantageous in use than the ordinary Turkey-red oils.

John Mercer (see p. 135) also made an oxidized sulphated oil, but by a somewhat different treatment.

Soluble Oil.

Under this name there are sold to dyers and cotton finishers two preparations, both based on the use of castor oil. The name which is given to them arises from the fact, that while they are liquids of an oily appearance they are freely soluble in water. They are used in various processes of dyeing and print-ing with alizarine dyes, direct dyes, etc., although usually the Turkey-red sulphated castor oils already noticed are preferred in the finishing of cotton cloths where a full and yet mellow feel is required. One of these preparations is sulphated castor oil, the other is practically a solution of castor-oil soap in water.

— The sulphated soluble oils are made by the same process as that for the Turkey-red oils, which has been already described,

only more water is added at the final stage to bring down the contents of castor oil to the standard of 25 per cent. Perhaps occasionally a little more soda is added to preserve the transparency of the liquor. Such a sulphated castor-oil soluble oil will contain :—

73·96 per cent. water.
0·74 ,, alkali.
23·74 ,, castor oil.
1·56 ,, salt and sodium sulphate.

These sulphated soluble oils may be distinguished from the saponified soluble oils (see below) by the fact that they contain much less alkali, as will be seen from the analyses that are given. Further, if the oil be evaporated to dryness and ignited, the residue, dissolved in water and acidified with hydrochloric acid, gives with barium chloride a white precipitate of barium sulphate.

Analysis of Turkey-Red Oil.

Water.—Five to ten grammes of the oil are weighed out in an evaporating basin and placed in a drying oven heated at 220° F. At intervals the basin and its contents are weighed, and when the weight remains constant the loss gives the amount of water present.

Other more complicated methods have been proposed, such as that of Ubbelohde, in which the oil is distilled with xylol saturated with water, but these offer no advantage over direct drying at 220° F.

Alkali.—Ten grammes of the oil are dissolved in water, a few cubic centimetres of an aqueous solution of methyl orange are added, and the solution titrated with standard sulphuric acid until the colour turns from yellow to red. The number of cubic centimetres of acid used multiplied by 0·031 gives the amount of sodium oxide (Na_2O) present.

If ammonia·has been used in making the oil, the quantity may be estimated by distilling the oil with caustic soda in a flask fitted with a delivery tube passing into a solution of sulphuric acid. 10 grms. of the oil are used; to this is added a

little caustic soda solution, and the mixture heated in a flask gently, so as to avoid much frothing. The ammonia gas which is evolved is received in 50 c.c. of normal sulphuric acid. At the end of the operation a few drops of phenol-phthalein solution are added, and the excess of acid titrated back with normal caustic soda. The difference between 50 and the number of cubic centimetres of alkali used, multiplied by 0·017, gives the quantity of ammonia (NH_3) present.

Total Fat.—The 10 grms. of oil used for determining the alkali may also be used for this test. A little more acid is added, the mixture is placed in a separating funnel, a quantity of ether (not petroleum ether) is added, and the whole mass well shaken. A strong solution of common salt is next poured into the funnel, and the whole allowed to stand for the ethereal-oil mixture to settle out. The under layer of water is run off, a fresh quantity of salt solution added, the whole shaken up, and again allowed to stand. The ethereal layer is run into a weighed beaker, the ether evaporated off on a water-bath, and the residual oil weighed. Carefully worked, this method gives good results.

Another method is as follows: 5 grms. of the sample are weighed into a beaker, diluted with water, and sufficient dilute sulphuric acid added to decompose the oil; 10 grms. of stearic acid, paraffin wax, or beeswax are next introduced. The whole mass is boiled until the fatty matter becomes clear, when it is allowed to cool. The cake of fat is removed from the beaker, the water is heated and any particles of fat caused to run together. The water is poured off, the beaker rinsed out with water, care being taken not to wash away the drops of fat, the cake of fat is put back into the beaker, and the whole dried on the air-bath. When dry, the beaker is weighed and its contents of oil and stearic acid ascertained; the weight of the latter deducted gives the amount of total fatty matter present in the original oil.

Sodium Sulphate.—The amount of sodium sulphate present in the oil can be determined by taking 10 grms., dissolving in ether, and extracting the ethereal solution several times with a pure saturated brine solution. The mixed brine extracts are

then filtered and the sulphate precipitated with barium chloride solution after acidifyi⌐₀ ... ⌐ᵈᵣochloric acid. The precipitate is filtered off, washed with water, dried, then burnt over a Bunsen burner in a weighed porcelain crucible, allowed to cool in a desiccator, and weighed. The weight of barium sulphate found multiplied by 0·609 gives the weight of sodium sulphate present.

Sodium Chloride.—This is not often present, but may occasionally occur if a solution of common salt has been used in washing the oil during its preparation and the wash-waters have not been properly drained away. To determine its amount 10 grms. of the oil are dissolved in water, dilute nitric acid added, and the oil which is separated out filtered off. The filtrate is boiled and a solution of silver nitrate added which causes the formation of a precipitate of silver chloride if salt be present in the oil. This precipitate is filtered off, washed with water, dried, ignited in a weighed crucible, allowed to cool in a desiccator, and weighed. The weight of silver chloride found, multiplied by 0·407, gives the weight of sodium chloride present in the oil.

Separation of the Fatty Matter.—The fatty matter, the total amount of which has been obtained in the manner described above, is present in the Turkey-red oil in three forms: first, neutral or unchanged oil; second, soluble sulphated fatty acids; and third, as free fatty acids,—the latter two being present in the oil, combined with the alkali. These three forms of the fatty matter may be determined as follows :—

Neutral Oil.—20 grms. of the oil are dissolved in water, 10 to 15 c.c. of ammonia added, and the free oil extracted in a separating funnel with ether. The ethereal solution is evaporated and the residual oil weighed. Lewkowitsch recommends the addition of 20 grms. of glycerine, but this does not appear to be necessary.

Soluble Sulphated Fatty Acids.—To determine these, 10 grms. of the sample are boiled with water and either hydrochloric acid or nitric acid for about an hour. The mixture is filtered through a wet filter-paper and the residual fat is washed with warm water, the washings being added to the filtrate.

From the filtrate the sulphuric acid present is precipitated out by the addition of barium chloride; the precipitate of barium sulphate is collected and weighed in the ordinary manner. From the weight which is thus obtained the weight of barium sulphate, due to the presence of sodium sulphate (see above), is first deducted, and the remainder multiplied by 4·725 gives the weight of sulphated oil present, calculated as sulphoricinoleic acid. This method of analysis depends on the fact that the boiling with the acids liberates the sulphuric acid of the oil in the free condition.

The fatty acids are obtained by difference—that is, the sum of the neutral oil and the soluble sulphated acids, as obtained in the last two tests, is deducted from the total fatty matter as previously obtained.

Sulphated castor oil may be distinguished from other oils by its high acetyl value, a value of 125 or over indicating castor oil. Another method, which is also quantitative, for the estimation of castor oil, has been devised by Lane ("Journ. Soc. Chem. Ind.," 1907, p. 597) and depends on the insolubility in petroleum ether of lead ricinoleate.

FINISHERS' SOLUBLE OIL.

Besides the soluble oil prepared by sulphating castor oil as described in previous sections (see pp. 137 and 146), there is used in the finishing of cotton prints and cloths a soluble oil, which is nothing more nor less than a solution of castor-oil soap. Castor oil differs from other oils inasmuch as its soap dissolves easily in water to a clear solution, which may contain as much as 25 per cent. of fatty matter and still be liquid. This is used in the finishing trade to impart a full, firm, and yet somewhat pliable feel to cotton cloths, and there are few, if any, substances better than a castor-oil soap for this purpose.

· This soluble oil is made in the following manner:—250 lb. of good seconds castor oil are mixed with 30 gals. of water, in which has been dissolved 40 lb. of 98 per cent. caustic soda; this is boiled until the oil is completely saponified and a clear transparent soap paste is obtained. This is now mixed with

cold water until the mass measures 100 gals., when the preparation will be finished and ready for use. Other oils cannot well be substituted for the castor oil, as they will not give clear solutions under the same conditions.

The use of caustic potash in place of caustic soda gives a more fluid preparation, but costs more. Castor oil, too, has an advantage over many other oils—cotton, rape, linseed or fish oils—in that it gives pale, straw-coloured, soluble oils, while those named tend to produce dark-coloured oils. In order to cheapen the cost, some makers have added a pale rosin to the castor oil; such preparations are, however, not satisfactory in use, for rosin soaps tend rather to darken in colour by the finishing operations through which the cotton is passed.

The analysis of these soluble oils follows on the lines of soap analysis (see p. 54); they can be distinguished from the sulphated soluble oils by three features, viz. the presence of free alkali, a larger proportion—2·0 per cent.—of combined alkali, and the absence of sulphuric acid. See the section (p. 147) on "Analysis of Turkey-Red Oil". The following are analyses of several commercial soluble oils made by the author:—

	1.	2.	3.
Water	73·80	72·36	79·54
Free alkali as caustic soda . .	0·24	0·32	0·31
Combined alkali as Na₂O . .	2·30	2·48	2·37
Glycerine	2·20	2·45	1·84
Oil	21·46	22·39	15·94

FINISHERS' SOAP SOFTENINGS.

In some classes of cotton goods the stiffness imparted by the starch necessary to fasten in the filling is not required, for some goods must have an appearance of fulness and still remain soft and pliable to the feel. In all cases where excellence is aimed at, some tangible example possessing the required qualities in a high degree is taken as a standard or pattern to imitate.

The bleacher tries in the goods mentioned to produce an effect as nearly as possible approaching the soft and kindly feeling of a kid glove.

There are many substances that possess the property of softening the stiffness of the starch mixtures, and many articles are sold under various names for this purpose. Commonest among these softenings are those of what may be called the soap class.

The composition of these soap softenings varies very much. Some are nothing but a jellified tallow soap made by boiling a good tallow curd soap with water; others may be better made and contain other ingredients besides the soap. There is a strong element of fashion in these products; some softenings appear to have a vogue for a time, then they disappear from the market and others take their place, perhaps in turn to be displaced by another preparation.

The following formulæ give details of the preparation of some of these soap softenings, but an intelligent maker can modify these to suit the particular kind of work his finishing customer wants to do :—

1.—Take 25 lb. good white tallow soap, cut into thin shavings, add 7½ gals. of water, and boil until the soap is dissolved, then allow to cool, and when nearly cold stir well until the soap sets.

2. Weigh out 12 lb. tallow and 8 lb. lard, mix with 2 gals. of water, heat until the fats melt, then add 3 lb. 98 per cent. caustic soda dissolved in 2 gals. of water, boil until the fats are saponified, then add sufficient water to make 10 gals. of soap paste, allow to cool, and then stir until thoroughly cold.

3. Take 30 lb. of cocoa-nut oil, melt over 3 gals. of water, and add 5½ lb. 98 per cent. caustic soda dissolved in 2 gals. of water, boil the mixture until the oil is saponified, add sufficient water to make 10 gals., and allow to cool, stirring well.

4. Take 30 lb. cocoa-nut oil and 5 lb. tallow, and saponify with 6½ lb. of caustic soda as above, add water to make 10 gals., and 5 lb. powdered French chalk.

Some makers also add such articles as glycerine, liquid glucose, dextrine, starch, etc. The chief features to have regard to are :—First, colour, as these soap softenings must

not have any colour, so that they will not tint in any way white or printed cotton goods. Second, smell, as they should not impart any odour, or lead to the development of any odour in the finished goods. Third, they should not contain any free alkali, for that might change the colours of any printed goods on which the softening is used.

For these reasons it is necessary to make them from good fats like tallow, lard, cocoa-nut, and palm-nut oils, that make white soaps, and care must be taken to make them neutral.

In the preparation of the better grades, some makers add such bodies as spermaceti, paraffin wax, Japan wax, or ozokerite.

It may be pointed out here that these soap softenings cannot be used with any finishing preparations containing zinc, calcium or magnesium chlorides or sulphates, as these curd out the soap in the form of grainy masses of insoluble zinc, calcium, and magnesium soaps, the formation of which destroys the finishing effect of the soap softening.

OIL AND FAT ANALYSIS.

It is not intended in this chapter to enter very fully into all the various tests that have been described and applied in the testing and analysis of oils, but simply to describe a few of the more simple and characteristic tests, so that oil users may be able to ascertain whether a sample of oil be pure, or whether it be a fit substance for the particular purpose for which it is to be used.

The practical analysis of oils is one surrounded by many difficulties, and to make a satisfactory analysis and to report on the purity of a suspected sample demands a large and varied experience among oils, an experience which it cannot be expected that an oil user should possess. It is therefore advisable to submit a suspected sample to a competent analyst, and it is desirable that such an analyst should have a special knowledge . of oils. In fact, it would pay large users of oil to make special terms with such analyst to test every batch of oil they have delivered to them, to see that it is what it is represented to be and that it is fit for use. In sending a sample to an

analyst to be tested, from six to eight ounces should be supplied, as satisfactory tests cannot be made with less. '

In judging the purity or otherwise of a sample of oil the following determinations should be made:—

       1st.   Specific gravity.
       2nd. Free acidity.
       3rd.   Saponification value or equivalent.
       4th.   Unsaponifiable matter.
       5th.   Titre.
       6th.   Iodine value.
       7th.   Refractive Index.
       8th.   Flash Point.

The fifth test is applicable solely to fixed oils, and the 8th to mineral oils or to mixed oils.

The methods of making these various tests will be described, and then a few special tests for certain of the oils will be noticed.

1. There are three ways of determining the **specific gravity** of a sample of oil—first by a specific gravity bottle or tube ; second, by a hydrometer ; third, by the Westphal specific gravity balance.

The first method is the most accurate. There is a great variety of apparatus made specially for the purpose. One of the best forms is shown in Fig. 8 and consists of a small thin glass bottle accurately stoppered, and the stopper has a small thin tube bored through it, so that it may be completely filled without any air bubbles.

100
Cᴿ
15%

Fɪɢ. 8.

The bottle is carefully filled with the oil to be tested, at a temperature of 60° F., taking care to avoid the formation of air-bubbles, the stopper is carefully inserted, the outside wiped clean and dry, and the whole weighed. The weight of water, at 60° F., the bottle holds is also ascertained. Then the weight of the oil is divided by the weight of the water the bottle holds, and the result is the specific gravity of the oil. Thus a sample of olive oil gave the following figures :—

Weight of bottle full of water   .   .   38·496 grms.

  ,,   ,,   .   .   .   13·496 ,,

Weight of water   25·000 ,,

Weight of bottle full of oil .   .   .   36·387 ,,

  ,,   ,,   .   .   .   13·496 ,,

Weight of oil   22·891 ,,

$\dfrac{22\cdot891}{25} = 0\cdot9156$ specific gravity of oil.

Sprengel's tube, which is a U-shaped tube with capillary tubes turned at the ends, is a very convenient piece of apparatus for the determination of specific gravities where only small quantities are available, or it is desired to find the gravity at a higher temperature than 60° F. The apparatus is used in the following manner :—It is first weighed, then filled up to the mark with water at 60° F., and weighed again. The tube, after being calibrated with water, should be cleaned out by first filling with methylated spirit, then with ether, and dried. It is then filled up to the mark with the oil at 60° F., and again weighed. If the gravity is to be determined at some higher temperature, it suffices to suspend the tube in a flask or beaker of water at that temperature, and keep it there for a short time, then take it out, dry the outside of the tube, and weigh.

The hydrometer (Fig. 9) method of determining specific gravity of oil is that most used by oil dealers and consumers, and it is carried out as follows :— The oil to be tested is placed in a cylindrical glass jar, the temperature adjusted to 60° F., and the hydrometer is immersed in the oil. The degree on the scale of the latter instrument, which is level with the surface of the oil, is the specific gravity.
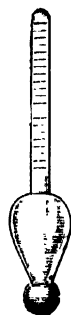
Fig. 9.

Hydrometers are made provided with a variety of scales, but what the oil tester wants is two instruments, one with a scale ranging from 0·700 to 0·860, and the other with a scale from 0·860 to 1·000. The latter includes all the fixed oils and the various grades of lubricating oils, and the former includes

all the gravities of the lighter naphthas and burning oils. As a rule, the two mentioned will be found sufficient, but if greater accuracy is required, then more instruments must be used to take the same range of gravities.

The special form of hydrometer frequently sold under the name of "oleometer" is perfectly useless, and should never be used. Its divisions are arbitrary, and nobody seems to understand them. This method of determining the specific gravity is subject to many defects. A large quantity of oil is required to float the instrument properly—a quantity which is not always available. The accuracy of the instruments, as ordinarily sold, is not to be depended upon, inasmuch as the scale is not adjusted for each particular instrument, and it is impossible to make two alike in every respect, and to have one especially graduated to ensure accuracy is a costly proceeding ; and there are other minor defects.

The Westphal balance method is a more accurate one, and is just as easy to work as the hydrometer, while the results are perfectly reliable. The Westphal balance is simple and easy to understand, and gives the specific gravity directly. The principal part of the apparatus is a glass bulb which has a volume of 5 c.c. Consequently, when immersed in water, it requires the balance arm to which it is attached to be loaded with a weight of 5 grms. to restore the equilibrium. In liquids of lighter gravity proportionately a smaller weight would be required, or in heavier liquids a heavier weight. Riders of 5, 0·5, 0·05, and 0·005 grms. are supplied, and with these the specific gravity is easily ascertained.

The position on the balance-arm of these weights gives the gravity at once, without any calculation being required. The balance is used as follows :—It is mounted in position, and by means of the regulating screw at the base of the balance, the two pointers are brought into line, with one another. Then the glass jar is filled with oil, and the glass bulb immersed in the latter. The large rider is now placed on the beam at the nearest division to produce equilibrium; then the next rider, and so on, until the two pointers are again brought into line.

Then the numbers of the divisions are read off in the order of the weights, and these give the specific gravity. Thus, supposing the largest weight was on the 9, the next on the 1, the next on the 8, and the smallest on the 3 divisions of the balance-arm, the specific gravity is 0·9183.

The glass plummet supplied with the instrument takes the form of a thermometer, the range of which is, however, only a few degrees on each side of 60° F. By substituting for this plummet one made of solid glass rod exactly 5 c.c. in volume, it is possible, with the Westphal balance, to obtain the specific gravity of oils at any temperature.

The balance does not give good results with very viscid liquids, like glycerine, thickened rape and cotton-seed oils, or cylinder oils; such liquids should be tested with the bottle.

Temperature is a very important element in testing the specific gravity of oils, and therefore the temperature of the oil at the time of testing must be noted. The standard temperature is 60° F. (15·5° C.), and, if possible, samples of oil should be brought to this temperature before testing. Temperature affects oils by decreasing the gravity as the temperature increases, and *vice versâ*. Although there are slight differences among the various oils as to the amount of variation brought about by temperature, yet these variations are slight, and, for the purposes of correction, may be neglected. The difference in the specific gravity of an oil for 1° F. is 0·00035, and for 1° C., 0·00063. Using these factors, correction for temperature may be made. Thus suppose an oil has a specific gravity of 0·918 at 64° F., at 60° F. its gravity will be 0·918 + (0·00035 × 4) = 0·9194. In other words, multiply 0·00035 by the number of degrees above or below 60° F., and add to or subtract from the specific gravity found according as the temperature is above or below the standard temperature of 60° F.

Too much stress must not be placed on the specific gravity test. Like most other oil tests, its indications are often of a negative character. It will not tell what an oil is, but what it is not. Thus it will not say that a given sample of sperm oil is pure, but it will say when an oil is not pure. Thus a sample

of oil, said to be sperm, may have the right specific gravity (0·880), but for all that it may not be pure, and other tests fhust be made to decide this point. On the other hand, suppose that this test shows it to have a specific gravity of 0·870, the oil may be immediately condemned as impure.

The determination of the specific gravity of solid fats, like tallow, palm oil, etc., is rather more troublesome than is that of liquid oils. A simple but only approximate method is to melt the fat at not too high a temperature. Then pour it into a specific gravity bottle, allow to cool down to 60° F. (15·5° C.), and weigh. This plan is objectionable on account of the great contraction which some fats undergo on cooling down, which may result in the bottle not being quite full of fat, and so a low and erroneous result will be obtained. Another plan is to have a wide glass tube, fitted with a cover which can be pressed down tightly. The glass is first weighed full of water, then cleaned and filled with the melted fat, which is allowed to cool down. The cover is put on and screwed down tightly, and the glass weighed again.

Another plan, which is greatly used, is to take advantage of the fact that fats or oils will just float in mixtures of alcohol and water of the same specific gravity. The *modus operandi* is as follows : The fat is just melted, and then allowed to drop into alcohol, whereby it is converted into spherical drops. Mixtures of alcohol and water of various gravities—0·945, 0·940, 0·935,

FIG. 10.

etc.—are employed. The globules of fat are dropped into each of these alcohol solutions until one is found in which the fat floats; the specific gravity of that alcoholic solution corresponds with that of the fat.

The best method is to use a bottle of the form shown in Fig. 10, filling it with the melted fat, and then, while it is suspended in a boiling water-bath, adjusting the level of the fluid fat to the mark. The flask is then allowed to cool, and weighed. It is calibrated before use by filling to the mark with distilled water at 15·5° C., and weighing. This

form of bottle may also be used for oils fluid at ordinary temperatures, and has this advantage in summer that, as the oil gets warm and expands, it does not run down the outside of the bottle as with the form shown in Fig. 8.

TABLE OF SPECIFIC GRAVITIES OF FATTY OILS AT 60° F. (15·5° C.).

Almond oil	0·919
Arachis (ground nut) oil	0·920
Castor oil	0·964
Cocoa-nut oil	0·925
Cotton-seed oil	0·923
Soya-bean oil	0·924
Linseed oil	0·932
Olive oil	0·915
Palm oil	0·940
Rape oil	0·914
Sesame oil	0·923
Lard oil	0·912
Tallow oil	0·912
Neatsfoot oil	0·914
Tallow	0·940
Sperm oil	0·883
Whale oil	0·925

In the summaries of the constants given under each oil, gravities at other temperatures are given.

2. **Free Acidity.**—It is important that lubricating oils should be free from acid, whether this be of fatty or mineral origin, as it has a destructive effect on the metal of machinery, and it is astonishing what a corroding effect a small quantity of free acid in oil has on metal, especially on brass or copper when the two bodies have been in contact for some time. If an oil containing 3 per cent of free acid be left in contact with brass for twelve hours it will have acquired a green tint, showing that it has dissolved some of the metal.

Fatty oils, such as olive, rape, castor, cotton, generally contain small quantities of free acid, rarely less than 1 per cent., but the writer has found as much as 22 per cent. of free fatty acid present in oils. This free acid may have been present originally in the oil owing to defective methods of extraction, or, if the sample be an old one, may have developed by keeping,

All fatty oils, on keeping for some time, slowly become rancid, some oils more rapidly than others. This rancidity is brought about by the combined action of the oxygen and moisture present in the air with which they are in contact, and results in the decomposition and splitting up of the oil into its two constituent parts, glycerine and fatty acid.

Mineral oils are usually free from acid. If any be present, it is most likely to be sulphuric acid, and indicates imperfect washing of the oil during the process of manufacture.

A simple test for the detection of acidity in oils is the following: Make a solution of phenol-phthalein in methylated spirit—as much of the former as will stand on a sixpence—in about 6 oz. of the spirit. Add to the solution a drop or two of caustic soda until the liquor has acquired a perceptible red tint. Then take a little of the oil to be tested, add a small quantity of the above test solution, and shake well. If there be any acid in the oil, the red colour of the test solution will be discharged. No other substance is capable of detecting traces of acid in oil. Litmus, which is much used by many persons, is of no use for this purpose.

The amount of free acid in oils may be readily determined, thus : 10 grms. of the oil are weighed into a clean glass beaker, and 10 c.c. of neutral methylated spirit or alcohol added with stirring, then 1 or 2 c.c. of the phenol-phthalein test solution. A standard decinormal solution of caustic potash or soda is then run in slowly from a burette, constantly stirring all the while until a permanent red colour is obtained. As each drop of alkali solution falls into the oil it produces a pink spot. As long as any acid is in the oil this disappears on stirring. As soon, however, as the acid is neutralized, the pink colour remains permanent. Each cubic centimetre of alkali solution used is equal to 0·0282 grm. of free oleic acid. The result multiplied by ten gives the percentage of acid in the oil.

If it is necessary to distinguish mineral acids from fatty acids in oil, a solution of methyl orange may be used. This is turned pink by mineral acids, such as sulphuric acid, but is not affected by fatty acids.

3. Saponification Value or Equivalent.—As has already been explained, the alkalies, caustic soda and caustic potash, convert the fatty oils into soap, but they have no action on hydrocarbon oils, except to form an emulsion from which the oil gradually separates out on standing.

Alkalies can be used in the testing of oils in three ways— to ascertain whether an oil is a pure fat or a hydrocarbon oil, or a mixture of both, and, in the first case, by noting differences in the colour and appearance of the soap formed, to determine the character of the fatty oil present.

. The method of applying this test is as follows :—A solution of caustic soda or caustic potash (the latter has the strongest action on oils and very often gives the best results) is prepared, having a specific gravity of 1·340 (68° Tw.). Two volumes of this solution are shaken up in a test-tube with four volumes of the oil. Fatty oils will combine with the alkali and form an emulsion, from which very little oil will separate on standing and the aqueous layer always has an emulsified appearance. Hydrocarbon oils only form a slight emulsion. The oil separates out on standing, leaving the aqueous layer quite clean, or with only a faint cloudy appearance. A mixed oil will vary in appearance according to the proportion of the two oils present: if hydrocarbon oils are in the larger proportion, they will form a layer on the top and the aqueous layer will be emulsified ; if the fatty oil is in the larger proportion, then it will often be difficult to detect the mineral oil, but a little experience with this test will soon enable users of it to detect small quantities of hydrocarbon oil. A method of detecting mineral oils in fatty oils, which is more certain, and will show 2 or 3 per cent., is to dissolve a piece of caustic potash about the size of a pea in 5 c.c. of alcohol, then add a few drops of the oil to be tested and boil for two or three minutes, and add three or four c.c. of distilled water. If the solution remains clear, only a fatty oil is present. Mineral oil causes the solution to be turbid, and even so small a quantity as 2 per cent. will show itself in this way.

The amount of mineral oil in mixed oils is best ascertained as follows: 25 grms. of the oil are mixed with 10 to 15 c.c. of

the caustic alkali solution and 25 c.c. of water and 5 c.c. of alcohol; the mixture is boiled, with constant stirring, for about an hour; by that time the fatty oil will be saponified. The mixture is then put into a separating funnel, and more warm water and 25 c.c. of petroleum ether added. The whole is shaken together for a few minutes, then allowed to stand, when it separates into two layers. The upper layer consists of the petroleum ether with the mineral oil; the lower is an aqueous layer containing the soap made from the fatty oil. This is run off, clean water added, the mixture shaken up and again allowed to stand, and the aqueous layer again run off.

This operation is repeated until the aqueous layer runs off clear. The ethereal layer is now run into the weighed flask, the ether distilled off, and the residual oil weighed. The weight multiplied by four gives the percentage of mineral oil in the mixture.

Koettstorfer's saponification test is one of the most important tests that can be applied to oils, fatty oils especially. This is carried out as follows : Two standard solutions are required, one of caustic potash dissolved in alcohol and containing about 28 grms. pure KOH in 1 litre of alcohol, the other is a solution of sulphuric acid containing 24·5 grms. H_2SO_4 per litre. Both these are what are called by chemists " semi-normal solutions ". An alcohol solution of phenol-phthalein is used as an indicator; this body is colourless, but alkalies make it of a deep red colour, which is destroyed by acids. The solution should be rendered of a faint pink tint by adding a drop or two of caustic potash.

Two grammes of the oil or fat are accurately weighed in a flask, and 25 c.c. of the alcoholic solution of potash are measured and added. The flask has fitted to it a long glass tube which acts as a reflux condenser. The flask, with its condenser tube and contents, is heated in a water-bath, the flask being shaken at intervals till the oil is thoroughly saponified, which will take place in about thirty minutes. The flask is then removed, and the contents allowed to cool.

A small quantity of the phenol-phthalein solution is added,

and the standard acid solution run in from a burette drop by drop until the red colour of the mixture disappears. Twenty-five cc. of the potash solution are boiled alone in a similar flask with a tube attached, for the same time, and also titrated with the standard acid. The difference between the two amounts of acid used shows the quantity of potash required to saponify the oil. This difference multiplied by 0·02805 gives the weight of KOH in grammes; this, multiplied by 100 and divided by the weight of oil, gives the weight of KOH (potassium hydroxide) required to saponify 100 parts of oil, and this multiplied by 10 gives the "Saponification Value" or milligrammes of potash per 1 grm. of oil.

Methylated spirit may be used for making the alcoholic solution of potash, providing it be purified by distillation over lime and caustic soda as follows :—

The spirit is first placed in a bottle with a small quantity of quicklime and a piece of caustic soda, and allowed to stand for twenty-four hours, being shaken up at intervals. The spirit is next transferred to a retort or flask, and a little fresh lime and soda added. It is then distilled on the water-bath till about 95 per cent. has come over; the remaining 5 per cent. is thrown away. This process frees the spirit from impurities which gradually act on the potash, and cause it to become dark brown, this coloration interfering somewhat with the operation of titration with the acid. A slight brownness does not make much, if any, difference. It disappears along with the red colour due to the phenol-phthalein at the end of the titration.

The reason for boiling 25 cc. of the potash alone is also due to the spirit or alcohol containing impurities which destroy the potash on boiling, and would therefore cause the oil to appear to have too high a saponification value; but this error is eliminated by the method of carrying out the test described above.

As a rule, oils that resemble olive oils require from 19 to 19·5 per cent. of potash, rape oils from 17 to 17·6 per cent., drying oils from 18·5 to 19 per cent., whale oils 18·75 per cent., solid fats like tallow 19·25 to 19·8 per cent., cocoa-nut oil 25·5 per

cent., butter 24 per cent., and sperm oils 12·3 to 14 per cent. of potash for complete saponification.

ɩ Adulteration of fatty oils with mineral oils would show itself by an abnormally low percentage of potash being required; and it would be possible to calculate the amount of adulteration from the figures which have been obtained, by multiplying the percentage of KOH absorbed, by 100 and dividing by 19,,when the approximate percentage of fatty oil in the sample will be obtained. The "Saponification Equivalent," or grammes of oil or fat saponified by 1 grm. molecule (56·1 grms.) of potash, may be found by dividing 56,100 by the "Saponification Value".

4. **Unsaponifiable Matter.**—This is determined by first saponifying 5 grms. of the oil or fat with alcoholic soda or potash, evaporating to dryness, dissolving the soap in water, pouring into a large separating funnel, and extracting three successive times with light petroleum ether. The ethereal extracts are mixed, washed with water, and transferred to a tared flask, the ether distilled off, and the residue dried in the oven at 105° C. until constant in weight. This residue multiplied by 20 gives the percentage of unsaponifiable matter in the oil.

The fact that the unsaponifiable matter of animal fats contains cholesterol, while that of vegetable oils and fats contains phytosterol, has been made the basis of a test for detecting the presence of animal fats in vegetable oils and fats, or vice versa. The original test proposed by Bomer ("Zeit. Untersuch. Nahr. Genussm," 1898, 81) consisted in saponifying the fat with alcoholic potash, and extracting the unsaponifiable matter with ether, which was then distilled off, and the residue recrystallized from alcohol. The process has been subsequently improved by converting the cholesterol or phytosterol into their acetic esters by heating with acetic anhydride, and determining the melting point of the resulting ester. Cholesteryl acetate melts at about 114° C., and phytosteryl acetate at 125° to 137° C., and according to Bomer, an acetate melting at 117⁵ to 118° C. corresponds to an addition of 1 to 2 per cent. of vegetable oil; at 120° to 121° C. to an addition of 2 to 3 per cent. vegetable oil; and

at 123° to 125° C. to an addition of 3 to 4 per cent. of vegetable oil. The following method for carrying out this test, which is known as the phytosteryl acetate test, is described by Revis and Bolton (Allen's " Commercial Organic Analysis," ii. p. 301.)

Fifty grms. of the clear fat are boiled with 75 c.c. of 95 per cent. alcohol, cooled, and the alcohol poured off, a second extraction being made with a further 75 c.c. of alcohol. These combined extracts, which will contain the greater part of the cholesterol and phytosterol and some fat, are transferred to a porcelain basin, and an excess of solid sodium hydroxide added, the mixture being then evaporated, with gentle stirring. After most of the alcohol has evaporated, more than sufficient sodium bicarbonate is added to convert the excess of sodium hydroxide into sodium carbonate, then some sand, and the whole evaporated to dryness, ground up in the dish, and extracted with light petroleum spirit. The residue from the ether is heated with 5 c.c. of (approximately) $\frac{N}{2}$ alcoholic sodium hydroxide solution, and again evaporated to dryness with sand. A fresh extraction with petroleum spirit is made, followed by evaporation, and the residue is taken up with the smallest possible quantity of absolute alcohol. If necessary, the solution is boiled with animal charcoal and some 95 per cent. alcohol, filtered, and evaporated to dryness. The crystals obtained are examined microscopically, cholesterol crystallizing in laminae, phytosterol in needle-shaped tufts; they are then converted into their acetate by boiling with acetic anhydride in a covered watch-glass, evaporating off the excess of acetic anhydride on the water-bath, and recrystallizing them from absolute alcohol, when the melting point is determined.

5. **Titre, or Solidifying Point of the Fatty Acids.**—This test, due to Dalican, consists in determining the solidifying point of the fatty acids separated from a fat or oil, a figure which is an important characteristic of most fats, and, in the case of tallows, is largely employed as the basis for their commercial valuation.

The test is carried out by first saponifying the fat with

alcoholic sodium hydroxide solution, decomposing the resulting soap with dilute sulphuric acid, and after washing and drying the liberated fatty acids, determining their solidifying point. Half an ounce of the sample is melted in a shallow porcelain basin on a water-bath, and 15 c.c. of a 25 per cent. solution of sodium hydroxide added, together with 25 c.c. of redistilled methylated spirit. The contents of the basin are now evaporated on the water-bath, with constant stirring, until a pasty mass of soap is formed, and this is redissolved in a further 25 c.c. of redistilled methylated spirit, and again evaporated to dryness on the water-bath. The solid soap thus obtained is dissolved in water, sufficient dilute sulphuric acid added to decompose it, and the whole warmed until the fatty acids melt to a clear oily liquid on the surface. The water underneath is now siphoned off, more distilled water added to wash out any remaining trace of mineral acid, and again siphoned off, this treatment being repeated until the washings are no longer acid to litmus paper. The melted fatty acids are next poured on to a dry filter-paper, which is inserted in a funnel resting on a beaker, and the latter is placed either in the water-bath, or in an air-oven at about 100° C., until the clear fatty acids have filtered through it.

From 10 to 15 grms. of these dry fatty acids are transferred to a wide test tube, about six inches long and one inch in diameter, which is inserted through a cork into a flask or wide-mouthed bottle, to protect the tube from draught. The tube is closed with a loosely fitting perforated cork, through which passes a short range thermometer (0° to 60° C.) accurately graduated in fifths of a degree and having its bulb just immersed in the fatty acids as near the centre as possible.

The temperature is now raised to a few degrees above the melting point of the fatty acids, and allowed to cool down without stirring. As soon as the fatty acids just begin slowly to solidify they are stirred round gently with the thermometer, the temperature on which will gradually fall till a minimum point is reached. Stirring is now discontinued, and the rise in temperature, which is usually produced by the heat given out by the acids in crystallizing, is observed. The maximum temperature

attained by the fatty acids during this rise is the "titre" of the sample.

6. Refractive Index.—This may either be determined directly by means of an Abbé total reflection refractometer, or an Amagat and Jean oleo-refractometer (" Analyst," 1890, p. 87) or the refractive power may be read off on an arbitrary scale by means of a Zeiss butyro-refractometer.

One of the great advantages of the test is the ease and rapidity with which it may be carried out, while a further advantage of the Abbé and Zeiss instruments is that only a very small quantity of the sample—five or six drops—is necessary.

The different forms of apparatus are fully illustrated and described in the catalogues of most firms supplying chemical apparatus, and it is therefore unnecessary to give a description here.

Different observers employ various temperatures for determining refractive indices, ranging from 20° to 60° C., but the International Conference on Food Analysis (" Analyst," Nov. 1911, 538) recommend the adoption of a standard temperature of 40° C.

7. Iodine Value.—If an oil is mixed with a small quantity of an alcoholic solution of iodine, the latter gradually becomes decolorized. This has been found to be due to the fatty acid of the oil absorbing the iodine and forming compounds with it. The fatty acids present in oils belong to four distinct series :— *One*, the stearic series, better known to chemists as the " acetic series." This series does not combine with iodine, so that the larger the proportion of the glycerides of these acids there is in an oil, the smaller the quantity of iodine with which it combines. The *second* series of fatty acids is the oleic series, each of which is capable of combining with iodine in the proportion of two atoms of iodine to one molecule of fatty acid. The *third* series is sometimes called the " tetrolic " or " linolic series," the members of which absorb four atoms of iodine for each molecule of fatty acid, and the fourth is the *linolenic* series, each of which absorbs six atoms of iodine per molecule. As the acids of these two latter series are characteristic of drying oils, it follows that

linseed and other drying oils absorb more iodine than any
other class of fatty oils.

     Hübl's Method.—Based on these principles is founded Hübl's
test, which has for its object the determination of the amount
of iodine absorbed by an oil. It is carried out as follows :—Five
solutions are prepared. 1st, a solution of 25 grms. of iodine in
500 c.c. of alcohol; 2nd, a solution of 30 grms. of mercuric
chloride in 500 c.c. of alcohol; 3rd, a solution of 10 grms. of
potassium iodide in 100 c.c. of water; 4th, a solution of 24·8
grms. sodium thiosulphate (hyposulphite) in 1000 c.c. of water
(each cubic centimetre of this is equivalent to 0·0127 grm. of
iodine) ; 5th, a solution of 2 grms. of starch in 100 c.c. of water.
Equal volumes of the iodine and mercuric chloride solutions are
mixed about twelve to twenty-four hours before use.

     From 0·2 to 0·5 grm. of the oil is weighed out into a tightly
fitting stoppered bottle and dissolved in 10 c.c. of chloroform.
For drying oils 0·2 grm. is sufficient; for other oils 0·3 to 0·5
grm. may be taken. Twenty-five c.c. of the mixed iodine solu-
tion are added, and the mixture allowed to stand in a dark place
for at least four hours. This will be long enough for non-drying
and semi-drying oils, but in the case of drying oils the oil should
be left in contact with the iodine solution for eighteen hours.
Similar quantities of the chloroform and iodine solution are
placed in another bottle to make a blank test. At the end of
the time, 20 c.c. of the iodide solution and 150 c.c. of water are
added, and the mixture titrated with the sodium thiosulphate
solution, until the yellow colour is nearly discharged, when a
few drops of starch solution are added, and the addition of thio-
sulphate continued until the blue colour disappears. The
difference in the number of c.c. of the sodium thiosulphate solu-
tion used in the two experiments, the blank test and the one
with the oil, represents the quantity of iodine absorbed by the
oil. This figure multiplied by the iodine equivalent of the
sodium thiosulphate solution (found by titrating it with a known
weight of pure resublimed iodine), and by 100, and divided by
the weight of fat taken, gives the iodine value of the fat.

     Wijs' Method.—The Hübl method has now to a very large

extent been displaced by the Wijs process, in which the iodine is absorbed by the fat much more quickly, only about thirty minutes' contact being required. The Wijs iodine reagent consists of a solution of iodine monochloride in glacial acetic acid, and may be prepared by either weighing out 7·9 grms. of iodine trichloride (which must be done in a weighing bottle), and 8·7 grms. of iodine, dissolving them separately in glacial acetic acid, mixing and making up to a litre with glacial acetic acid, or by dissolving 13 grms. of iodine in a litre of glacial acetic acid, and passing a current of dry chlorine into the solution until the iodine is all converted into the iodine monochloride—a point which may be determined by the gain in weight, or with a little practice, by the change in colour of the solution from brown to yellow. The details of the process are exactly similar to those in the Hübl method, except that it is preferable to dissolve the fat in carbon tetrachloride instead of in chloroform.

TABLE GIVING THE IODINE VALUES OF A NUMBER OF FATS AND OILS.

Oil.	Iodine Value.
Linseed oil { Baltic	195-204
Linseed oil { Indian	180-190
Linseed oil { American	175-186
Cotton-seed oil	104-110
Thickened Cotton-seed oil	50
Rape oil	99-102
Thickened Rape oil	456
Soya-bean oil	131-158
Castor oil	83-86
Olive oil	80-83
Arachis oil	86-98
Corn, or Maize oil	116-123
Lard	59-63
Tallow	39-44
Cocoa-nut oil	8·5-9·5
Palm-kernel oil	10-13
Palm oil	51-52
Chinese Vegetable Tallow	30-32
Hypogaeic acid	100
Oleic acid, pure	89·7
Oleic acid, commercial	80-84
Ricinoleic acid	85
Linoleic acid	201·5

Hydrocarbon oils are also capable of absorbing iodine and bromine, the quantity absorbed being dependent upon the proportion of olefines the oils contain. Paraffins have no affinity for iodine or bromine: hence American oils, containing as they do more paraffin than Scotch shale oils, absorb less than the latter as a general rule. The following table gives a few iodine values of petroleum and shale products :—

Name of Oils.	Iodine Equivalent.
Scotch shale oil, 886	23·5
„ „ 890	20·6
„ „ 908	23·2
„ „ 863	29·2
„ „ 873	26·0
American petroleum oil, 905	9·7
., „ 916	7·8
„ „ 911	8·1

Bromine Absorption.—This is similar in principle to the iodine absorption, and though numerous processes, both gravimetric and volumetric, have been proposed for its determination, it has now been almost entirely superseded by determination of the iodine absorption. The following gravimetric method of determining the bromine absorption was devised by O. Hehner, ("Analyst," 1895, p. 50).

A small, wide-mouthed flask is carefully weighed, and from 1 to 3 grms. of the fat introduced into it. These are dissolved in 10 c.c. of chloroform, and then pure bromine is added, drop by drop, until the bromine is decidedly in excess. Both the chloroform and the bromine must be previously tested in a blank experiment, to make sure that they leave no appreciable residue on heating. The flask and its contents are then heated on the water-bath till most of the bromine is driven off, a little more chloroform is added, and the mixture again heated, the chloroform vapour helping to drive out the excess of bromine. Then the flask and its contents are placed in an air-bath regulated at about 125° F., and kept there until repeated weighings show their weight to be constant; this takes several hours. Some acroleine and hydrobromic acid escape during the drying. The increase in weight is the amount of bromine

absorbed. This process gives very satisfactory results. The writer has obtained the following figures from different oils :—

Menhaden fish oil	.	.	.	43·6	per cent.
Pale seal oil	.	.	.	87·6	"
Pale whale oil .	.	.	.	4·6	"
· Scotch cod oil .	.	.	.	59·9	"
Japan fish oil .	.	.	.	123·3	"
Arctic sperm oil	.	.	.	59·9	"
Straw seal oil .	.	.	.	137·2	"
Olive oil .	.	.	.	51·3	"
Lard	.	.	.	.	40·6	"
Butter	.	.	.	.	21·6	"
Castor oil .	.	.	.	43·7	"
Linseed oil (raw)	.	.	.	114·2	"
Linseed oil (boiled) .	.	.	60·0	"
Linseed oil (boiled) .	.	.	112·(	"

8. **Flash-Point Test.**—This is one of the most important tests to apply to mineral or mixed lubricating oils. It is most easily carried out in the following way : —

Procure a white porcelain basin of about 2 oz. capacity, or, what is better, a copper vessel, and support it by suitable means over a Bunsen burner, nearly fill it with the oil to be tested, and hang a thermometer in the oil. The bulb of the latter should be completely covered by the oil, while it should not be allowed to touch the bottom or sides of the basin. Connect with another gas supply an ordinary mouth blow-pipe, and adjust the supply of gas to this so that the flame at the jet is only about the size of a small pea. Then heat the oil, carefully adjusting the size of the Bunsen flame so that the heating of the oil is not carried on too rapidly; a rise of 10° F. per minute is the generally recognized amount of heating, and it is not advisable to exceed this amount. A slow rate gives much more accurate results than a quick rate of heating.

During the progress of this test three points can be observed : first, the vaporizing point; second, the flash point; third, the burning point or fire test.

The Vaporizing-Point.—This is the first point to be observed. It is the temperature at which a vapour begins to be perceived. This is also known as the "smoke-point." As a rule, it is not

considered of much importance, and what particular value it has is somewhat uncertain. Of course oils with a low vapor-izing temperature, say of less than 150° to 160° F., would be unpleasant to work with on machinery where that temperature is likely to be exceeded.

The method of carrying out and the rapidity of heating have a considerable influence on the temperature at which an oil will begin to give off vapour. If the basin is heated rapidly over a naked flame, the temperature of vaporizing will be much less than when the basin is heated on a sand-bath. A difference of 20° or even 30° F. may often be obtained by these two different methods of heating the oil. Those dealers and consumers who attach particular importance to the smoke point always immerse the basin of oil in a deep sand-bath, taking care that it is well surrounded with sand. It is only by this means that different observers can obtain concordant results on the smoke-point.

The Flash-Point.—If, while the oil is being heated, the small gas jet is applied at intervals, say, every two or three degrees rise in the temperature, taking care not to let the flame touch the surface of the oil, soon a blue flame will be observed to shoot across the surface of the oil. The tempera-ture at which this flame is first seen is the flash-point.

Whether a sand-bath or a naked flame is used for heating the oil makes but little difference in the flash-point, rarely more than what different observers would note with the same oil. The higher the flash-point the safer is the oil to use, because then there is less chance of it giving off an inflammable vapour at any temperature to which it may be subjected in actual use.

This point of inflammability is of particular importance to cotton mills, where such a large quantity of fluff is always about the machinery. If an oil with a low flash-point were used, and the temperature should by accident get above the flash-point and a light come in contact, it is quite possible that the oil would catch fire, and this would be sure to spread through the fluff, and hence, probably, through the mill, so

that it is of particular importance in a cotton mill to use an oil
with a sufficiently high flash-point. 350° F. is quite a safe
point, and there is no necessity to much exceed it. Some
dealers pride themselves on the high points of their oils, but
a high flash-point is not all that is wanted in an oil. There
is the proper viscosity to be considered, and, generally speaking,
high flash-points and high viscosities go together; thus where
you want, as in spindle oils, a moderate viscosity only, you
cannot have very high flash-points; and if the latter feature
only is considered, then an oil may be used which, owing to its
high viscosity, is not the most suitable for the purpose. For
use in cotton and other textile mills, where the peculiar
conditions and material introduce a special element of danger,
the oils should not flash at a lower temperature than 350° F.,
while for all other mills and works 330° F. may be accepted as
a safe point. For cylinder oils 500° F. is the lowest flashing-
point usually accepted as safe, but in the case of oils for
lubricating cylinders there cannot be any question of safety,
because they are used under such circumstances as to preclude
any idea of their taking fire. The true test of the value of
a cylinder oil is its having a good viscosity which it does not
lose to any great extent on being heated.

There is, however, a connection between a high flash-point
and a high viscosity in cylinder oils. The process of manu-
facture consists in eliminating all light portions, the presence of
which would reduce the flash-point and the viscosity consider-
ably. The flash-point is much easier to ascertain than the
viscosity, and for this reason, not for any considerations of
safety, attention is given to it in the case of cylinder oils.

The Burning Point.—This is known in America as the "fire
test." If after the flash-point has been determined the
heating of the oil be continued, it will be observed that the
flashing becomes more frequent and the flame gets more
luminous. Presently the flame, instead of going out, will
continue to burn. The temperature at which this occurs is
" the burning point," or " fire test." This point is not regarded
as of very much use in this country, nor, indeed, is it; but in

America it is considered of quite as much importance as the flashing-point.

The following table gives the three points for the chief varieties of hydrocarbon oils :—

	Degrees Fahrenheit.		
	Vaporizing Temperature.	Flash-Point.	Burning-Point.
Scotch shale oil, 865	178	318	382
„ „ 875	184	330	406
„ „ 885	203	353	420
„ „ 890	230	376	448
American petroleum oil, pale, 885 . . .	...	...	...
„ „ 903-907 . .	210	392	458
„ „ 915 . .	220	442	488
„ „ 920 . .	234	428	484

	Degrees Fahrenheit.		
	Vaporising Temperature.	Flash-Point.	Burning-Point.
American petroleum oil, cylinder . . .	266	462	...
„ „ . .	270	528	...
Russian petroleum oil, pale, 896 . .	190	348	410
„ „ 908 . .	210	384	470
„ „ 914 . .	230	390	496
„ „ 910 (residuum) .	180	320	385
Rosin oil, 985	190	320	385

The method of ascertaining the flash-point described above is known as "the open flash test." There is another mode of carrying out this test known as the "closed flash test." The oil is heated in a metal vessel fitted with a cover in which are two apertures—one for the thermometer, the other aperture is fitted with a sliding cover. The oil is heated in the usual way. When heated to within a few degrees of its flash-point, the sliding cover is drawn on one side and the test flame inserted. If no effect is produced, the flame is withdrawn, the sliding cover replaced, and the heating continued. These operations are repeated at intervals of every two or three degrees until, on the introduction of the test flame, a flash or slight explosion is observed. The temperature indicated by the thermometer is noted as the flash-point. The flash-point by the close test is always slightly lower than by the open test.

It makes but little difference with what apparatus the open

test is carried out, whether with large or small quantities of oil, provided the rate of heat is not too rapid.

The closed flash test, however, varies with the construction of the test apparatus, and the quantity of air in proportion to the oil, so that it is necessary to use a standard apparatus.

The best instrument for the determination of the flashing-point of lubricating oils by a close test is Gray's. This in-
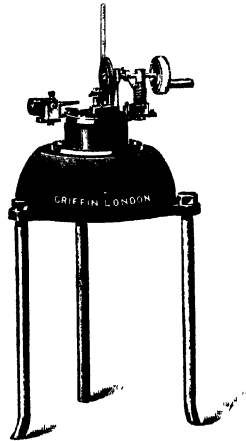
Fig. 11.

strument consists of a brass cup of the same size as that used in the Government standard petroleum tests, viz. 2 in. in diameter by $2\frac{2}{10}$ in. in depth. A line cut round the inside of the cup, $1\frac{1}{2}$ in. from the bottom, indicates the height to which it is to be filled in testing oil. The cup is closed by a tightly fitting cover, through the centre of which a small shaft or spindle passes to the bottom of the cup, carrying two sets of stirrers, one of which is below the surface of the oil, the other in the vapour space above. On the top of the spindle, above the lid, a small bevelled wheel with a milled edge is fixed, which gears with a vertical bevelled wheel on the inner edge of a horizontal shaft carried on two standards fixed on the lid, and terminating at the outer end in a disc of non-conduction material in which is fixed a handle for rotating the shaft. There are four openings in the

lid. Through one a thermometer is inserted to indicate the temperature of the oil. The remaining three provide means of producing the flash. One of these is immediately in front of the small tilting jet which ignites the gases. The other two, one on each side, admit air to produce the explosive mixture. These parts are normally closed by the loose three-quarter disc flat cover, provided with openings which, when the cover is turned one quarter round, coincide with the ports in the fixed lid.

In using this instrument the cup is filled to the mark with the oil to be tested. The test jet is lighted; the flame being adjusted to about $\frac{1}{8}$ in. in size. Heat is applied below the oil cup by a gas or spirit flame, either direct or through the medium of a sand-bath, and the temperature of the oil raised at the rate of 10° to 15° F. per minute, the stirrers being turned at short intervals during the process of heating.

When nearing the point at which the oil is expected to flash, it is advisable to reduce the rate of heating in order that observations may be more accurately made.

The test for flashing-point is made by drawing the horizontal shaft, which has about $\frac{1}{3}$ in. end play, outwards, which puts it out of gear with the stirrers and in gear with the sliding cover, which, being partly turned, opens the ports and tilts the flame of the test jet into the centre one. If gas is present in sufficient quantity, a slight flash with an explosion is produced; if not, the ports are automatically closed, the heating is continued, the stirrers being used, and the test for "flash" repeated at intervals till the flash is observed, the temperature at which this occurs being taken as the flashing-point of the oil.

Among the less frequently used methods of examination of oils and fats may be mentioned :—

Sulphuric Acid Tests.—There are two different tests which can be made by means of sulphuric acid on oils. One is a colour test, the other is a temperature test.

(1) *Colour Test.*—This is a most useful test for fatty oils,

but one where great experience and a close observant eye are required. This test must only be carried out in bright daylight, so that shades of colour can be clearly discerned. It quite fails when done by gaslight or a dull daylight.   •

The *modus operandi* can be varied somewhat, but it is essential in applying this test that it should always be made in the same manner, as the results are slightly different if the manner of making the test is varied. A good method is to place twenty drops of the oil in a clean white basin, and then add two drops of strong sulphuric acid. As the acid falls through the oil, streaks of colour show themselves, and a tint of characteristic colour gradually spreads through• the oil. After a minute or two the oil and acid can be stirred together and the colour again noted. This test should first be made with samples of known purity, so as to gain some experience of it, and when testing unknown samples comparative tests with pure oils should also be made. Vegetable oils give various colours, usually shades of yellow, brown, or green; fish oils turn of a violet or purple colour; animal oils turn red or reddish-brown. Hydrocarbon oils turn a blackish-brown, but this effect is usually very slight.

The experimenter had best construct his own table of shade of colour. It is very difficult to convey by words what is actually meant by a colour name.

(2) *Temperature Test.*—This is known as Maumené's test, and is a very useful test, and one that is easily made. Twenty c.c. of the oil are measured into a small beaker, and a thermometer placed in it and its temperature noted. Eight c.c. of strong sulphuric acid. sp. gr. 1·845, are then added, and the oil and acid thoroughly stirred together with the thermometer, as long as the temperature is observed to rise. The highest point which is reached is noted, and, the initial temperature being subtracted, the difference will be the increase in the temperature caused by the action of the acid on the oil, and it will be found that•the different oils show certain variations in the amount of increase they produce, as seen in the following table :—

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Oils.	Increase in Temperature.	
	Degs. C.	Degs. F.
Olive oil	44	79·2
Sperm oil	37	66·6
Rape oil	35	63·0
Rape oil (thickened)	58	104·4
Cotton-seed oil	65	117·0
Neats'oot oil	32	57·6
Tallow oil	38	67·6
Castor oil	56	97·2
Rosin oil	25	45·0
Petroleum lubricating oil . . .	25	54·0
Scotch shale oil	6	11·0
Linseed oil	68	122·4

These figures have been obtained by the writer when work-ing with this test. It will be noticed that there is a marked difference between mineral oils and fatty oils, the former giving much lower figures than the latter; and between drying and non-drying oils, drying oils yielding much higher figures, the action being more energetic, and generally there being a quan-tity of sulphurous acid gas evolved (distinguished by its odour of burning sulphur); differences may also be noticed when carrying out this test on the colour and consistence of the resulting mass which may be utilized as qualitative tests for the oils. The thickened rape and cotton oils are more heating than the normal oils. These figures must not be taken as a standard of comparison, but they are simply given to show the general tendency of this valuable test. It is found that different observers obtain slightly different figures, although their own figures are concordant enough. This is due to slight differences in the conditions of carrying out the test, which will naturally vary with each observer. Hence this test must be conducted in a comparative manner, samples of unknown purity with samples of known purity.

With this test it is possible to ascertain approximately the proportion of the constituents of a mixed oil when those con-stituents are known; thus, supposing an oil consists of a mixture of cotton-seed and olive oils, it will yield an increase of temperature between 44° and 65° C., according to the

relative proportions of the two. This is worked out by a
formula—

$$X = \frac{(C - B) \times 100}{A - B}$$

Where X = Percentage of oil A in sample.
  „ A = Mean rise for pure sample of oil A.
  „ B =   „   „   „   „   B.
  „ C = Observed rise in the mixed sample.

Thus, supposing in a mixture of olive oil and cotton-seed oil
the observed rise was 56° C., then, according to the above
formula, we have—

$$\frac{(56 - 44) \times 100}{65 - 44} = \frac{12 \times 100}{21} = 57 \cdot 1 \text{ per cent. of oil A.}$$

Then there are 57·1 per cent. cotton-seed oil, and 42·9 per cent.
olive oil in the mixed sample.

By dissolving the oil in an inert solvent, such as carbon
tetrachloride, the rise in temperature produced by adding sul-
phuric acid is approximately proportional to the iodine value.

Tortelli ("Chem. Zeit." 1909, 125) has improved on this process
by adding the acid to the oil in a vacuum jacketed tube. He
employs 5 c.c. of sulphuric acid, sp. gr. 1·8413 for 20 c.c. of
oil, and deduces the following relations between the Maumené
value and the iodine value.

For non-drying oils, Maumené value × 1·82 = Iodine value.
  „ Semi-drying oils,   „   „   × 1·60 =   „   „
  „ Drying oils   „   „   × 1·48 =   „   „

• *Valenta's Acetic Acid Test.*—If equal volumes of glacial
acetic acid and a fatty oil be mixed together and then heated, a
clear solution will be obtained. On allowing to stand, a cloud
will in a short time make its appearance in the liquid. Valenta
discovered that this cloud makes its appearance at different
temperatures with different oils, the " turbidity temperature," as
it is called, being the point to be ascertained. Valenta's work
has been more or less confirmed by subsequent observers, but
still there are differences in the recorded observations which
serve to show that there are several modifying circumstances
in the application and carrying out of the test which must be

taken into account. The strength of the acid is important. The temperature at which the turbidity is obtained is distinctly higher with a weak than with a strong acid; a dry test-tube or glass is necessary to obtain satisfactory results. Rinsing with water must be avoided, as the small quantity of water left in the glass will affect the subsequent tests. Slight differences are also observable by variations in the manner in which the test is made.

The author has obtained the following results with this test, using 5 c.c. of the acid and oil, very convenient quantities, in a wide test-tube, the thermometer being immersed in the oil during the whole of the operation :—

Oil.	Turbidity Temperature. Centigrade.	Oil.	Turbidity Temperature. Centigrade.
Colza	99	Rape	90
Castor	Soluble at ordinary temperature.	Ground nut	72
Neatsfoot	85	Lard	76
Cotton-seed	63	Olive	76
Sperm	85	Whale	71
Oleic acid	Soluble at ordinary temperature.	Ox	48

A slight modification of the process, devised by Pearmain and Moor, is to weigh out 2·75 grms. of the fat or oil into a short stoppered tube, and add 3 c.c. of glacial acetic acid. The tube is then stoppered and heated in a water-bath, the temperature being raised until the contents of the tube become clear on shaking, after which the source of heat is removed, and the tube allowed to cool down gradually in the centre of the water-bath until the contents again become slightly turbid. The temperature at which this takes place is recorded, and is a fairly definite figure for any given oil. The following are figures obtained by Pearmain and Moor, employing this method :—

Lard	97-99
Tallow	96-99
Cotton-seed oil	71-89
Sesame oil	90-97
Olive oil	88-91

Bromine Thermal Value.—When an oil is combined with bromine a certain amount of heat is generated, and in the case of most oils there is a relationship between the rise of temperature produced, and the iodine value of the oil, so that this ratio having once been ascertained for the apparatus employed, the iodine value may be readily calculated from the rise in temperature observed on adding the bromine.

This has been recommended by Hehner and Mitchell ("Analyst," 1895, xx. 146) as a rapid means of ascertaining the degree of unsaturation of oils and fats, a weighed quantity of the oil being dissolved in chloroform or acetic acid and the rise in temperature on adding bromine noted. The oil, chloroform, and bromine are first brought to the same temperature, 1 grm. of oil dissolved in 10 c.c. chloroform in a Dewar's vacuum jacketed test-tube, and 1 c.c. of bromine added from a special pipette, consisting of a 1 c.c. pipette with a narrow tube, bent twice at right angles, connected to its top, the horizontal portion of the tube containing caustic lime kept in position by asbestos plugs. The mixture is immediately stirred, and the rise in temperature measured with a thermometer graduated in fifths of a degree.

Melting-Point of Fats.—The most convenient way of ascertaining the melting-point of fats is that known as the capillary tube method. This is carried out in the following manner: A piece of thin glass tubing is drawn out at one end into a capillary tube. The fat or substance whose melting-point is required is heated in a small glass beaker until it is just melted, and the end of the capillary tube dipped into the melted fat; some will be taken up. The tube is withdrawn and placed on one side for some time to cool, to allow the fat to solidify. The capillary tube is next tied to the stem of a thermometer, in such a way that the bulb and capillary tube where the fat is are close together. A beaker of cold water is placed on a sand-bath, and heated by a Bunsen burner. The thermometer is suspended in the centre of the water. As long as the temperature remains below the melting-point of the fat, the latter will be opaque and stationary, but when the melting-point is reached, then the fat becomes transparent, and will rise in the tube. When this event is

noticed, the temperature is read off on the thermometer, and this gives the melting-point of the fat.

Reichert's Test.—Some fats, notably cocoa-nut oil, palm-nut oil, butter, and whale oil, contain fatty acids which are soluble in water, and, when distilled along with water, volatilize and distil over, the distillate having an acid reaction. It has been found possible to employ this process as a test in the examination of oils, and as it was originally devised by Reichert, is known by his name. Since its first introduction, other analysts have published sundry modifications in the manner of carrying it out, notably that of Wollny, and that of Polenske.

Reichert's test is carried out in the following manner :— 2·5 grms. of the oil or fat are thoroughly saponified by boiling with ·25 c.c. of a normal, or nearly so, alcoholic solution of caustic potash, in the same manner as is adopted for the Koettst-orfer value. After the saponification is complete, boil until all the alcohol has evaporated, then dilute with water, add sufficient dilute sulphuric acid to decompose the soap, add water, if necessary, to bring up the volume to 75 c.c. ; then distil in a retort until 50 c.c. have come over, taking care to avoid bumping over of the liquid. Should the distillate be cloudy, or show the presence of fat globules, filter it, washing the filter with warm water. Then titrate the clear distillate with deci-normal caustic soda, using phenol-phthalein as an indicator, and noting the number of cubic centimetres of the alkaline solution required.

The following are a few figures obtained with this test :—

Fat or Oil.	Number of Cubic Centimetres of $\frac{N}{10}$ KOH used.
Butter	12·5 to 15·2
Cocoa-nut oil	3·5
Palm-nut oil	2·5
Palm oil	0·8
Whale oil	3·7
Sperm oil	1·7
Cotton-seed oil	0·3
Castor oil	1·4
Thickened rape oil	1·2
Thickened cotton-seed oil . . .	1·3

Some tests are only applicable to individual oils. Such, for example, are the

Elaidin Reaction, or Poutet's test, which was first devised in 1819, and is of very great value in judging the purity of olive oil. Many methods of applying the test have been proposed, the best, due to Archbutt, being to make use of a reagent prepared by dissolving 18 grms. of mercury in 15·6 c.c. of cold nitric acid of 1·42 specific gravity. The solution is best effected in a glass tube kept cool by immersion in water. The test solution should have a green colour. Archbutt used 96 grms. oil to 8 grms. of reagent, but 50 c.c. of oil to 2 c.c. of solution a very convenient quantity to take. The oil and solution are taken together in a wide mouthed bottle, and allowed to stand, the shaking being repeated at intervals of ten minutes for two hours, and the temperature being kept constant at not less than 5° C. The time taken to solidify, the consistency of the mass, and also its colour, are noted.

Archbutt gives the following particulars of results obtained by this test : —

Oil.	Time to Solidify.	Colour of Mass.	Consistence.
Olive . . .	60 minutes . .	Canary yellow	Hard and impenetrable.
Oleic acid .	50 minutes . .	Lemon yellow	Penetrable.
Nut . . .	60 to 90 minutes .	Lemon . .	Soft.
Neatsfoot . .	180 minutes . .	, .	Penetrable.
Rape . . .	More than 6 hours	Deep orange .	Apparently solid, miscible with water.
Bottlenose .	160 minutes . .	Deep Lemon .	Soft.
Southern sperm	No solid, but thick in 6 hours . .	Orange . .	Buttery.
Ground-nut .	...	,, .	Soft.
Cotton . .	...	,, .	Turbid, fluid.
Niger . .	...	,, .	Thin fluid.
Cod-liver . .	...	Blood red .	Fluid.
Castor . .	...	Lemon . .	Like oil.
Sesame . .	...	Orange . .	Thick, but fluid.
Menhaden .	...	Dark red .	Turbid.

Halphen's Test for Cotton-seed Oil.—Equal parts of the oil or fat (or its fatty acids), amyl alcohol, and a 1 per cent. solution of sulphur in carbon bisulphide, are heated together in a

test-tube placed in a boiling water bath until effervescence ceases, and then transferred to a boiling brine bath for about an hour, when, if cotton-seed oil is present, a pink coloration is produced. The reaction may be rendered much more rapid, according to Rupp ("Zeit. Untersuch. Nahr. Genussm.," 1907, xiii. 74), by heating the mixture in a stoppered flask, while according to Gestaldi ("Chem. Centr.," 1912, 758), the reaction may be rendered sufficiently sensitive to detect as little as 0·25 per cent. of cotton-seed oil, by substituting pyridine for the amyl alcohol, the test being carried out by adding 1 drop of pyridine and 4 c.c. of the 1 per cent. solution of sulphur in carbon bisulphide, to 5 c.c. of oil, and heating the mixture in a water-bath for 30 minutes.

THE END.

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